

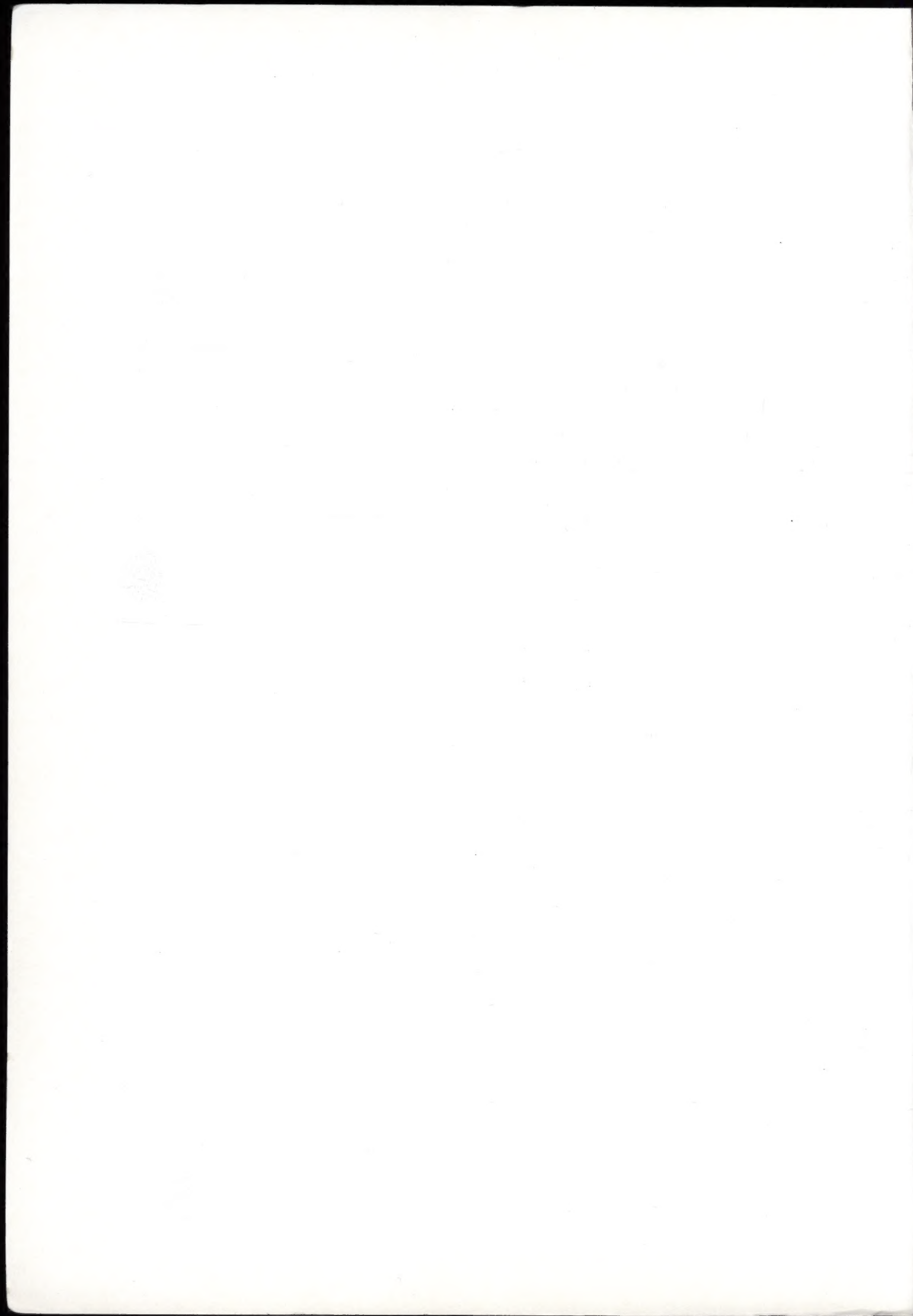
ICOM COMMITTEE FOR CONSERVATION

8th Triennial Meeting
Sydney, Australia
6–11 September, 1987

Preprints Volume II



COMITÉ DE L'ICOM POUR LA CONSERVATION



PHOTOGRAPHY IN THE ARCTIC

The first point of view on photography in the Arctic is that of the explorer. A number of the first explorers, such as Parry, Ross, and others, have left behind them a valuable record of the Arctic region. Their photographs, which were taken with the aid of the daguerotype, are now preserved in the archives of the British Museum. These photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

Photography in the Arctic is also of great value to the explorer. It gives him a record of the country which he is exploring. It also gives him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

Photography in the Arctic is also of great value to the explorer. It gives him a record of the country which he is exploring. It also gives him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

The first point of view on photography in the Arctic is that of the explorer. A number of the first explorers, such as Parry, Ross, and others, have left behind them a valuable record of the Arctic region. Their photographs, which were taken with the aid of the daguerotype, are now preserved in the archives of the British Museum. These photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

Photography in the Arctic is also of great value to the explorer. It gives him a record of the country which he is exploring. It also gives him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

Photography in the Arctic is also of great value to the explorer. It gives him a record of the country which he is exploring. It also gives him a record of the people who live in the Arctic. The explorer's photographs are of great value to the explorer, as they give him a record of the country which he is exploring. They also give him a record of the people who live in the Arctic.

A NOTE ON THE COVER

The bark painting, ochre on stringybark, is by the late Declan Apautimi of the Tiwi tribe, Bathurst Island, N.T. The artist has duplicated ceremonial arm-bands, "palmatjintas," and a forked throwing stick, "miluanta," with landmarks of a particular ceremonial site. These decorations and objects are strongly influenced by the components and myths associated with the "pukamani" mortuary ceremony.

Photography by Jennifer Steele. Reproduced by permission of the Aboriginal Artists Agency, Sydney.

The hornbill wood carving (back cover) was made by the Abelam people of Papua New Guinea. The hornbill is an important totemic figure in the Abelam ceremonies and is normally attached to the façade of men's spirit houses used for secret initiation rituals.

Photography by the Australian Museum. Reproduced by permission of the Australian Museum.

NOTE EXPLICATIVE SUR L'ILLUSTRATION EN COUVERTURE

Le tableau peint sur écorce d'eucalyptus, ocre sur écorce filandreuse, est l'oeuvre de feu Declan Apautimi, de la tribu Tiwi de l'île Bathurst, T.N. Cet artiste a recréé des brassards de cérémonie, "palmatjintas", et un bâton projectile fourchu, "miluanta", orné de points de repère d'un certain site consacré aux célébrations rituelles. Ces décorations et objets sont grandement influencés par les composantes et les mythes liés au rite funéraire "pukamani".

Photographie: Jennifer Steele. Reproduction faite avec l'autorisation de l'Aboriginal Artists Agency de Sydney.

La sculpture sur bois du calao (en dos de couverture) a été exécutée par le peuple Abelam de Papouasie Nouvelle-Guinée. Le calao se veut une représentation totémique importante dans les célébrations rituelles des Abelams. Elle est généralement fixée à la façade des maisons des esprits, réservées aux rites secrets d'initiation chez les hommes.

Photographie: The Australian Museum. Reproduction faite avec l'autorisation de l'Australian Museum.

ICOM COMMITTEE FOR CONSERVATION
Preprints 1987

THE UNIVERSITY OF CHICAGO

LIBRARY

ICOM COMMITTEE FOR CONSERVATION

8th Triennial Meeting
Sydney, Australia
6–11 September, 1987

Preprints

THE GETTY
CONSERVATION
INSTITUTE

Los Angeles
1987

ACKNOWLEDGEMENTS

The conference organizers gratefully acknowledge the following sponsors for their generous support: Art Gallery of New South Wales; Department of Special Minister of State, Australian Commonwealth Government; ICCROM; National Maritime Museum; Office of the Minister for the Arts, N.S.W.; Wild Heerbrugg AG and Ernst Leitz (Wetzlar) GmbH in association with Wild Leitz (Australia) Pty Ltd.

Also, Abbey Chemical Agencies Pty Ltd in association with Minolta Camera Company Ltd; Art Gallery of Western Australia; Australian Museum; Australian National Commission UNESCO; British Council; Edwards Dunlop and B. J. Ball; International Cultural Corporation of Australia Limited; Museum of Applied Arts and Sciences.

And, in fine, Australian National Gallery; Australian War Memorial; A.W.A. Computers; Conservation Resources International; Grace Fine Art; National Australia Bank Limited; National Gallery of Victoria; Percy Marks Pty Ltd; S & M Supply Company Pty Ltd.

EDITOR

Kirsten Grimstad

ASSISTANT EDITOR

JoAnn Hill

DESIGN

Sheila Levrant de Bretteville

PRODUCTION

Leslie Stone

Debbie Swanson

Copyright © 1987
International Council of Museums
Copyright of individual papers
remains with the authors
Published by the Getty
Conservation Institute, 1987,
on behalf of the ICOM Committee
for Conservation
ISBN 0-89236-094-1
Printed in the United States
of America

Available from:

International Council of Museums
1 rue Miollis
75732 Paris Cedex 15
France

ICCROM
13 via di San Michele
00153 Rome
Italy

The Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, CA 90292-6537
U.S.A.

Contents/Table des Matières

Volume II Working Group 10

Stone/Matériaux pierreux

- 437 Josef Riederer, Coordinator, *Triennial Overview*
- 439 Neville Agnew, James Druzik, Thomas Caperton, and Michael Taylor, *Adobe: The Earliest Composite Material*
- 447 O.P. Agrawal, Tej Singh, B.V. Kharbade, Kamal K. Jain, and G.P. Joshi, *Discolouration of Taj Mahal Marble—A Case Study*
- 453 O.P. Agrawal, Tej Singh, and Kamal K. Jain, *Study on the Weathering of Taj Mahal Marble*
- 457 M. Aslam, M. Laurenzi Tabasso, P.L. Bianchetti, and A. E. Charola, *Studies of Lime Plasters and Mortars of the Taj Mahal*
- 465 Zdravko Barov, *An Effective Cleaner for Organic Stains on Stone*
- 469 G. Biscontin, A. Masin, R. Angeletti, and G. Driussi, *Influence of Salts on the Efficiency of a Conservative Siliconic Treatment on Stones*
- 475 Andreina Costanzi Cobau, *A Structure of Tuff Blocks: Treatment for Display*
- 479 M.C. Ganorkar, T.A. Sreenivasa Rao, and M. Bhaskar Reddy, *Deterioration and Conservation of Calcareous Stones*
- 487 Janusz Lehmann, *The Methodology for the Cleaning and Desalting of Stone Objects in Gołuchów Castle Museum*
- 493 Roberto Nardi, *The Conservation Intervention on the Arch of Septimius Severus in the Roman Forum*
- 503 Roberto Nardi, *Consolidation of a Mudbrick Wall Using Simple Technics and Materials*
- 509 Tadateru Nishiura, *Laboratory Test on the Color Change of Stone by Impregnation with Silane*
- 513 Ross Taylor, *The Conservation of St. Mary's Church Balmain, Sydney—The Approach and Analysis*
- 517 O.V. Yakhont, V.N. Yarosh, M.I. Filimonova, *Certain Investigations of Fragments of the St. George Sculpture from the Kremlin Museums, Moscow, with a View to Ascertaining Their Authenticity*

Working Group 11

Theory and History of Restoration/Théorie et histoire de la restauration

- 523 E. van de Wetering, Coordinator, *Triennial Overview*
- 525 Stefan C. Arteni and Myriam Sanchez-Posada de Arteni, *Peinture, restauration, et société*
- 533 Ivan Bentchev, *The Restoration of the Wall-Paintings in the Church of St. Nikita at Čučer/Macedonia in 1483–1484*
- 539 Laura Drysdale, *The Isolated Conservator*
- 545 L.A. Lelekov, *Professional Ethics in Restoration*
- 549 Krasimira Lukicheva, *Artistic Expertise and Restoration*

- 553 Hiltrud Schinzel, *Paint is Not Painting*
- 555 Władysław Ślesięński, *Theory of Conservation in Poland after 1945*
- 561 E. van de Wetering and D. H. van Wegen, *Roaming the Stairs of the Tower of Babel: Efforts to Expand Interdisciplinary Involvement in the Theory of Restoration*
- 567 Anneke Weersma, *Some Theoretical Considerations on the Handling and Care of Sacred Objects in a Museum Context*
- 571 O. V. Yakhont and L. N. Rastorguev, *On the Application of Indirect Data in Restoration Research*
- 573 O. V. Yakhont, *Problèmes de copies dans la conservation contemporaine des monuments*
- 577 N. N. Zhukova, *The First Research Institute for Restoration and Conservation of Archaeological Finds in the USSR*

Working Group 12

Care of Works of Art in Transit/Protection des oeuvres d'art pendant le transport

- 583 Sarah Staniforth and Peter Wilson, Coordinators, *Triennial Overview*
- 585 Timothy Green, *Shock and Vibration—Test Results for Framed Paintings on Canvas Supports*
- 597 Stephen Hackney, *The Dimensional Stability of Paintings in Transit*
- 601 Christine Leback Sitwell, *Vibration Test Results on an Air Ride Suspension Vehicle and Design Considerations for a Racking System*
- 607 Deborah Stewart, *Conservation in the Service of Mobile Exhibits*
- 611 Ola Westerudd, *Transportation and Handling of Art and Other Exhibits*
- 617 Peter Wilson, *Mathematical Predictions of Transit Case Performance; "Topplability," Thermal Insulation, Weight and Volume*

Working Group 13

Natural History Collections/Collections d'histoire naturelle

- 623 Robert Waller, *An Experimental Ammonia Gas Treatment Method for Oxidized Pyritic Mineral Specimens*

Working Group 14

Graphic and Photographic Documents/Documents graphiques et photographiques

- 633 Françoise Flieder, Coordinator, *Compte rendu triennal*
- 635 O. P. Agrawal and D. G. Suryawanshi, *Further Studies on the Problems of Conservation of Birch Bark*
- 641 Ildikó Beöthy-Kozocsa, Teréz Sipos-Richter, and Györgyi Szlabey, *Report on Parchment Codex Restoration by Parchment and Cellulose Fibre Pulp*
- 649 M. G. Blank and S. A. Dobrusina, *Estimation of Paper Stability*
- 653 Anne Cartier-Bresson, *Techniques d'analyse appliquées aux photographies d'Eugène Atget conservées dans les collections de la ville de Paris*
- 659 Bernard Guineau et Vincent Guichard, *Identification de colorants organiques naturels par microspectrométrie Raman de résonance et par effet Raman exalté de surface (S.E.R.S.), exemple d'application à l'étude de tranchefiles de reliures anciennes teintées à la garance*
- 667 Klaus B. Hendriks and Lincoln Ross, *Further Experiments on the Restoration of Discolored Black-and-White Photographic Images in Chemical Solutions*
- 671 Judith H. Hofenk de Graaff, *The Development of Standard Specification for Permanent Records in the Netherlands*

- 677 Bertrand Lavedrine et Françoise Flieder, *Les négatifs altérés par un traitement à l'iodure mercurique: analyse et restauration*
- 685 Françoise Leclerc, Françoise Flieder, et Frédéric Bulle, *Le colmatage mécanique des documents: Effet de l'incorporation d'un adhésif dans la pâte à papier*
- 697 Yu. P. Nyuksha and L. E. Sergeeva, *Paper Lamination: Biological Aspects*
- 701 Nathalie Ravenel et Cristina Danti, *Restauration et conservation des "Vues d'Italie," papiers peints en grisaille de Dufour et Leroy (1823) conservés au Palais d'Arco à Mantoue*
- 709 Wilma G. Th. Roelofs, Pieter B. Hallebeek, Judith H. Hofenk de Graaff, and Riet F. S. Karreman, *The Analysis of Natural Dyestuffs and Organic Pigments: A Comparative Study into the Possibilities and Limits of Various Methods*
- 719 Ingrid Rose, Yvonne Efremov, and Mihai Lupu, *Microscopic Examination of Works of Art on Paper during Treatment in Order to Determine the Effects of Treatment Methods on Fibers and Pigments—A Joint American-Romanian Research Project*
- 727 H. Stachelberger, A. Haberditzl, G. Banik, F. Bauer, and F. Mairinger, *Electrophoretic Investigations on Parchment Decay*
- 731 Janet L. Stone, *Treatment of 19th Century Tracing Papers from the Frederick Law Olmsted Collection*
- 739 Mariagrazia Plossi Zappalà et Antonio Zappalà, *Influence du contenu en plomb sur la conservation du papier*

Working Group 15

Mural Paintings and Mosaics/Peintures murales et mosaïques

- 749 Marcel Stefanaggi, Coordinator, *Activités du groupe de travail "Peintures murales et mosaïques"*
- 751 Cristina Danti, Fabrizio Bandini, et Guido Botticelli, *Méthodologie et application pratique de la séparation d'une peinture à l'huile sur mur d'une peinture à fresque sous-jacente*
- 759 S. V. Filatov, *Technique of Exfoliating Later Paintings from Wall Paintings in Oil*
- 763 Márta Járó et László Kriston, *L'analyse des pigments bruts romains découverts à Balaca*
- 765 András Morgós and József Lőcsei, *The Application of a Pre-Stressed, Curved, Rigid Support in the Restoration of an 18th c. Secco Painted on a Wagon Vault*
- 771 R. Pancella, V. Furlan, F. Girardet, et M. Stähli, *Conservation de la fresque de Hans Erni au musée d'ethnographie de Neuchâtel—Suisse—études préliminaires*
- 779 Walter Schudel, *L'usage de "colle-photo" dans la restauration des peintures murales*

Working Group 16

Resins: Characterization and Evaluation/Résines: caractérisation et évaluation

- 783 E. De Witte, Coordinator, *Triennial Overview*
- 785 G. Biscontin, C. Botteghi, C. Dalla Vecchia, G. Driussi, G. Moretti, and A. Valle, *Stability Study of Siliconic Resins Employed in the Stone Conservation*
- 791 E. René de la Rie, *Research on Picture Varnishes: Status of the Project at the Metropolitan Museum of Art*
- 797 Dominique Fromageot et Jacques Lemaire, *Un réexamen des propriétés de durabilité des "nylons solubles"*
- 805 Tadateru Nishiura, *Laboratory Evaluation of the Mixture of Silane and Organic Resin as Consolidant of Granularly Decayed Stone*

- 809 Barbara A. Ramsay-Jolicoeur, *An Investigation into Resin Coatings: Study of Naturally-Aged Examples*
- 817 Wilma G. Th. Roelofs, Riet F. S. Karreman, and Judith H. Hofenk de Graaff, *Research on the Analysis of Varnish Mixtures as Used on Old Bowed Instruments: Possibilities and Limits*
- 829 Norman H. Tennent and Joyce H. Townsend, *The Relevance of Preferential Surface Yellowing in the Light-Aging of Polymers for Conservation*
- 833 S. Walston, D. Horton-James, and S. Zounis, *Investigation into Methods and Materials for the Adhesion of Flaking Paint on Ethnographic Objects: A Progress Report*

Working Group 10

Stone

Matériaux pierreux



MEMBERS

R. Bugini (Italy)
R. van Grieken (Belgium)
L. Lazzarini (Italy)
E. Leary (United Kingdom)
M. Lebel (USSR)
J. Lehmann (Poland)
H. Materna (Germ.Dem.Rep.)
K. Niesel (Germ. Fed. Rep.)
E. Orcsik (Hungary)
R. Rossi-Manaresi (Italy)
E. Sagortschewa (Bulgaria)
R. Snethlage (Germ. Fed. Rep.)
J. Sramek (Czechoslovakia)
T. Stambolov (The Netherlands)
M.L. Tabasso (Italy)
A. Tucci (Italy)
E. de Witte (Belgium)

TRIENNIAL OVERVIEW

Coordinator
J. Riederer
(Federal Republic of Germany)

Assistant Coordinator
E. Charola
(Argentina)

PROGRAMME 1987-1989

1. All informations concerning the restoration and conservation of stone objects in museums shall be collected. Informations obtained from the work on buildings and monuments shall be evaluated with respect to treatment which can be used for indoor monuments.
2. Guidelines for the restoration and conservation of stone objects in museums shall be set up. During the last three years informations on cleaning and the removal of salts have been collected. During the next three years the joining of broken pieces and the consolidation of fragile surfaces will be treated.
3. An annual bibliography of publications concerning stone conservation will be set up.

SUMMARY

During the last three years the working group of stone had three meetings at Copenhagen (1985), Lausanne (1985) and Bologna (1986). It was decided that only a small group of specialists actively contributing to the working group of stone shall be considered as ordinary members. More than one hundred colleagues, which are informed by the newsletter and which contribute to the aims of the working group, are corresponding members, since their activity is more in the field of the restoration of building and not so much the work on museum objects. By that the working group of stone has first of all the function to extract from the enormous activities on the field of stone conservation those informations which are of interest for museums.



SUMMARY

ADOBE: THE EARLIEST COMPOSITE MATERIAL

Work in progress from two concurrent programs of research on adobe is outlined. A five year field experiment under the supervision of New Mexico State Monuments (NMSM) is to derive results for future restoration projects and provide base line data for new construction; laboratory work at The Getty Conservation Institute (GCI) is investigating high performance polymer systems applied to adobe.

Neville Agnew, Queensland Museum, Australia
James Druzik, The Getty Conservation Institute, USA
Thomas Caperton & Michael Taylor, New Mexico State Monuments, USA

Introduction

The global use of adobe or mudbrick, from ancient times to the present day, has been due no doubt to the ubiquity of raw material from which could be fashioned, in many guises and with different regional techniques, a functional composite material. The essential ingredient - wet mud, clay, earth - has been modified by man over the millennia in many ways. Sand has been added to improve compressive resistance and restrict cracking as the material dried; straw, dung, blood and other binding have all been used. Straw, in particular, was used in antiquity and continues to be used today. Indeed, the Israelites as brickmakers in Egypt placed store by it and the eventual consequences of it being denied them were dire [1]. There seems, though, to be little benefit in its use other than as a facilitator of crack-free drying [2]. All of these modifications of the raw material were empirical, derived by rule of thumb, to provide a workable, useful building material in which the properties of the final product were greater than the sum of those of the constituents. Thus, adobe is the earliest of mankind's composite materials, dating from the dawn of history [3] and, with little modern modification it is as geographically widely used today, perhaps even more so, as it was in the past. It is estimated [4] that at present some 30% of the world's population lives in dried mud dwellings.

It is our belief that too often in the past research projects on adobe have not been sufficiently sustained, which is why we see a collaboration of the GCI with NMSM, with its ambitious five year monitoring program of test walls, as being capable of yielding substantive results. We present here preliminary results of the two projects and outlines of projected work.

Fort Selden Test Wall Project

Test walls at Fort Selden State Monument in southern New Mexico were created to monitor, over five years, erosional rates and various methods used in adobe preservation.

Fort Selden is located near Las Cruces, New Mexico. The fort was established in 1865 to provide protection for the settlers of the Mesilla Valley. Upon abandonment in 1891, the army stripped the fort of salvageable lumber including the roofs. As a result the adobe walls have remained exposed to the weather for nearly 100 years (Fig. 1).

Preservatives Study

Two adobe walls, each 65 feet (19.8m) long and five feet (1.52m) high were built in an L-configuration providing exposed surfaces facing the four cardinal directions. Eleven treated wall panels (both plastered and unplastered) were applied to each wall face including two controls with and without the inclusion of straw. Straw was not included in the preservative treated panels. In total, 52 panel applications were made, each five by four feet in size (Fig. 2). Some panels were used for applications at 5% and 10% concentration. Table 1 outlines the treatments.

Basal Wall Treatment

Twelve walls, each with a different foundation, were constructed to determine the rate of capillary rise of water. Treatments were selected from modern and historic practice, as well as opinion, folklore and myth. Treatments included rock, gravel foundations, standard stem walls, sub-surface plastic aprons and French drains (Fig. 3).

Wall Cap Experiment

One wall, 20 feet long was constructed with four different caps consisting of stabilized adobe brick running along the same direction as the other wall bricks, stabilized adobe brick set at right angles to the wall providing a drip-edge set away from the surface, a cement cap, and a brick coping. These four caps are being monitored to determine to what degree erosion occurs where the cap meets the adobe wall.



Fig. 1 Fort Selden State Monument today.



Fig. 2 Fort Selden Test Wall Project.

Monitoring System

The panels are photographed bi-monthly in black and white and color. Bi-annually color video documentation is taken. Erosion is monitored, in part, with aluminum pins set flush to the plastered surface and moisture sensors have been placed in the center of the walls at two-course intervals sub-surface and above the surface. Weather is being recorded by a station provided by the US Parks Service and Munsell Soil Color notations are made bi-annually.



Fig. 3 Capillary moisture rise monitoring.

Observations After the First Year

In the field, erosion is graded by a five level system which has been strongly defined. In Table 2, this system (very little, little, moderate, serious, very serious erosion) has been reduced to numeric representation. By averaging across one is able to establish a tentative ranking and by summing down can infer the facing direction of greatest severity (ignoring for the moment any variability in application) which correlates somewhat with weather patterns. Table 3 groups the first year's performance and correlates rank order with the application methodology.

At this juncture a few interesting points are just emerging. So far asphalt emulsion (often used in manufacturing commercially available adobe brick) is doing quite well - neatly positioned between the high-solids content polymer emulsion systems. The control panels differ very little whether they incorporate straw or not and are gravitating downward, along with a plant extract, a mineral sealer and linseed oil. Interestingly, spray applications which should not perform as well as deeper bulk impregnation are already beginning to show evidence of exfoliation.

It is too soon to judge the capping experiments, but the capillary-rise walls all show significant subsurface moisture although no detectable moisture may be evident above ground. In fact it is surprising how little above-surface moisture occurs within the test walls - with the exception of the two walls having an above-surface concrete apron. Here moisture rises until it can escape over the top of the concrete.

THE GETTY CONSERVATION INSTITUTE STUDY

In the following discussion the terms preservative, consolidant, stabilizer, protectant and amendment are used as described by Spry [8]. This part of the paper reports the results of the first round screening of preservatives. From this point a second round testing of the best candidates, coupled with a study at a fundamental level (SEM, DTA/TMA, polymer-clay interactions and so on) prior to field testing by NMSM, will be done.

Research Design

A number of working suppositions were made prior to the laboratory study - some were subsequently modified in light of the results. These were:

- 1) Adobe, as a composite material, is porous, soft, wettable, and when wet its compressive strength is reduced (Fig. 4). The case of absorption-desorption by clay minerals and the consequent swelling-shrinking cycles cause cracking, and it is this that is responsible for much of the weathering and structural decay of adobe. Thus, there is a need to prevent, or limit, the hydration of clay which occurs when water penetrates an adobe structure and when water vapour permeates the porous material by diffusion.
- 2) It is desirable that the strength and cohesiveness of adobe, both wet and dry, be increased.

Both of these requirements can be met, in principle, by chemical preservation with polymeric systems.

- 3) Field treatments of adobe have usually attempted surface coating and water-proofing. These, inevitably, fail when water penetrates the core of the structure and abscission occurs between the more-or-less hydrophobic "skin" (which may be quite thick) and the wet clay. Water can penetrate via breaks in the outer layer and, more importantly, by capillary rise of ground water. Hence, surface coatings seem likely to

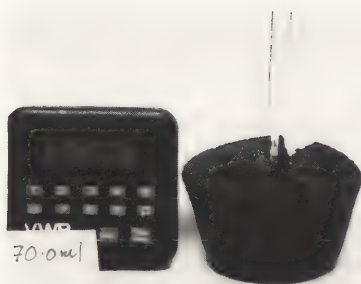


Fig. 4 Untreated block breaking up after dropwise addition of 70 ml water over 67.5 minutes.

be of little or no value in the long term and may, in fact, accelerate destruction when internal wetting occurs. It follows that complete or at least substantial impregnation is necessary (in the absence of other measures such as protective shelters) if durable preservation of outdoor structures is to be hoped for. By complete is meant infiltration throughout the object, but not necessarily void or pore filling, although some filling may occur.

- 4) Low viscosity is clearly of importance in achieving thorough infiltration and concentrations of polymeric preservatives greater than, say, about 10% would likely not infiltrate well for reasons of rapidly increasing viscosity. Thus, monomeric and prepolymer systems were of particular interest, as were techniques such as in situ precipitation polymerization.

Further, given the requirements above, it was advisable in the initial laboratory stage of screening preservatives, one against the other, that the system be kept simple and that as many variables as possible be eliminated. It was clear that there was a need to standardize on one adobe type and composition, and on the methods used for preparing test blocks, infiltrating solutions, and, as far as possible, on the testing and evaluation procedure. Details are given in the experimental section.

EXPERIMENTAL

Test Blocks

Raw adobe was obtained from a borrow pit adjacent to the historic Olivas Adobe in San Buenaventura north of Los Angeles. It was screened (3mm mesh) to remove coarse particulates, and sand:silt:clay fractions were determined [9] as 0:60:40% by volume. Clean silica sand (120-180 mesh) was added to give a test material of composition 40:36:24%. These blocks (truncated cones 40±2mm high by 50±2mm and 41mm dia.) were prepared by adding water (1 vol.) to the mixture (2.5 vols.) and casting in greased containers. Cylindrical samples, 36 x 130mm long, were also prepared. After 110 hr. at 50°C blocks were abraded (100 grit paper) to remove any release agent and fines from the surface. After equilibration at 45% RH/22°C for 7 days - during which time weight increased by 1% - the blocks were numbered, weighed, and infiltrated. Linear shrinkage during drying was 5-8%; blocks were homogeneous, crack-free, but with some small (2mm) air pockets.

Mineralogy

The adobe soil was qualitatively characterized by X-ray diffraction and wet chemical tests. It consists of quartz, plagioclase, potassium feldspar and mica as the major constituents with a mixed-layer clay illite/smectite and kaolinite as minor constituents. Because of the smectite fraction the adobe would be expected to show marked swelling-shrinking with changes in water content. The smectite group (to which montmorillonite belongs) characteristically displays this behaviour. No soluble inorganic salts were found, but there is evidence for soluble polymeric organic material - presumably humic acid. A reversible weight loss of 2.5% occurs on drying at 120°C, implying loss of water only and without change to the clay structure. At 800°C in air the weight loss is 7%, presumably due to loss of absorbed and claybound water plus organic material.

Infiltration Procedure

Triplicates were prepared for each system. After some trials the procedure was adopted of standing test blocks in preservative in covered beakers to a depth of about half their height. When capillary infiltration had reached near the top surface the block was inverted to 5-10 min. Blocks were drained, wrapped in aluminum foil and allowed to stand in the hood to equilibrate, usually overnight; they were then unwrapped and cured to constant weight at 50°C (Fig. 5). Some variation in procedure was used depending upon the nature of solvent and system. Surface coated blocks were immersed twice (10-15 sec.) and then treated as above.

Test Procedures

Three test procedures were developed:

- 1) Cured blocks were immersed in 1% aqueous surfactant (Micro laboratory detergent) at 50°C for 16 hr. followed by drying at 50°C for a similar period. Water uptake and loss was



Fig. 5 Infiltrated test blocks curing.

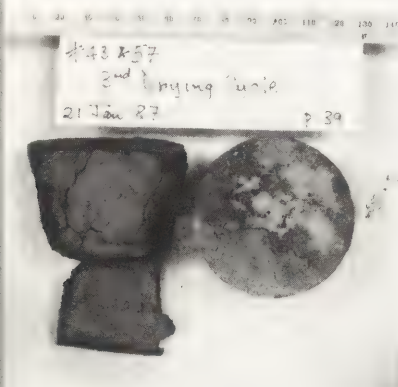


Fig. 6 B-72/MTMOS test blocks after third wet/dry cycle.



Fig. 7 Acryloid A-11 cylinder after the sixth cycle.

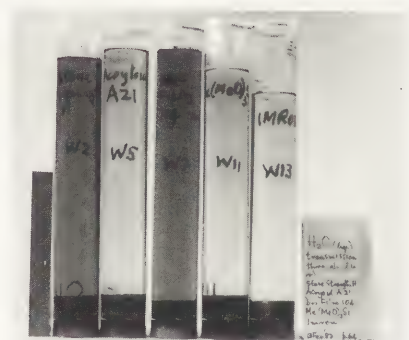


Fig. 8 After 13 days, 1 to r: SSH, A-11, DriFilm 104, MTMOS, PHDI.

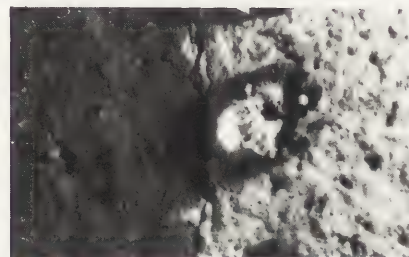


Fig. 9 DriFilm 104 abscission layer. (Water drop beads on treated layer only.)

determined by weighing. Cycling was repeated until failure, severe cracking or erosion occurred (Fig. 6). Test blocks were photographed.

One of each triplicate block was sectioned vertically and the surface stained with aqueous Methylene Blue to determine depth of penetration, internal wetting behaviour and any development of an abscission layer between infiltrated region and unconsolidated core.

- 2) Infiltrated cylinders were immersed to a depth of 35mm in 5% w/v sodium sulphate at 50°C for 16 hr. followed by drying at 50°C for a similar period. In final cycles cylinders were dried at room temperature to allow the hydrated salt to crystallize slowly (Fig. 7).
- 3) Liquid water transmission through cylinders (32 x 39mm dia.) was measured as a function of time at room temperature. Test samples were glued into the ends of clear plastic tubes (292 x 44mm i.d.) using neutral-cure silicone (Silastic RTV 737). Tubes were filled with water, sealed with Parafilm (with a needle prick air-hole) and stood on paper towelling to wick transmitted water away from the face of the sample and preclude the possibility of clogging at the surface by organic material as the water evaporated (Fig. 8).

Chemical Systems

Table 4 gives details of the systems used (a few minor systems based on aqueous emulsions and colloidal silica were briefly explored but were discarded when it became apparent that the water infiltrated the adobe much more rapidly than did the consolidant).

RESULTS

Results are summarised in Tables 5,6,7. These represent, in some instances, three trials each on three test blocks. Where inconsistencies appeared in wet-dry cycling the best results are reported as being representative of the true capability of the system.

DISCUSSION

Percentage weight gain from polymer loading in a matrix is not, in our view, a significantly relevant parameter in the first round comparative testing of one preservative against another. That is, if, say, polymer A is deposited in the test block to 1% mass increase while B has 4% and if A then performs the same as B in wet-dry cycling it does not necessarily follow that A is four times better than B, but only that A is likely to be better than B. There could be many reasons for the difference in performance: differences in hydrolytic stability, interactions of polymer with matrix - as in coating the clay particles, molecular weight difference, and other subtle effects, such as strength of chemical bonding to clay. However, if A appears better than B it is obviously worth attempting to optimise the deposition of A in the matrix in the hopes of increasing protective performance. For these reasons undue attention was not paid at this stage to the quantitative aspects of deposition in test blocks.

Most of the silicon based preservatives developed cracks during wet-dry cycling, though blocks held together. SSOH was the worst in this regard and cracks developed during curing. DF104 was impervious to cycling being extremely hydrophobic; but sectioned blocks with an unconsolidated core on repeated wetting showed the potential for surface spalling very well as an abscission layer formed between the wetted and hydrophobic regions (Fig. 9). MTMOS and SSH performed well - the latter marginally better; it also had the advantage of not forming a dark, brittle skin of polymer. The lower molecular weight prepolymer reactive silicone resin systems (H40, 290 Siloxane and DF1048-283) did poorly. The reason for this is not yet clear.

Among the acrylics Acryloid A-11 and A-21 were impressive while B-72 was poor. It seems that in the mixed B-72 - MTMOS system the acrylic was not contributing to the resistance to wet-dry testing. In sectioned blocks there was evidence of chromatographic separation of B-72 and MTMOS, but this was not investigated. Conservators using this and related systems on stone should

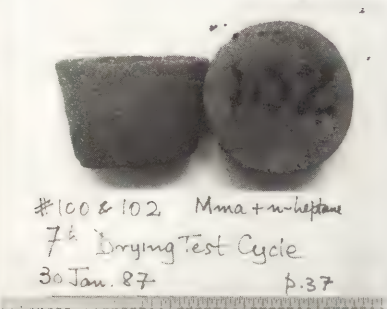


Fig. 10 PMMA precipitation polymerization.

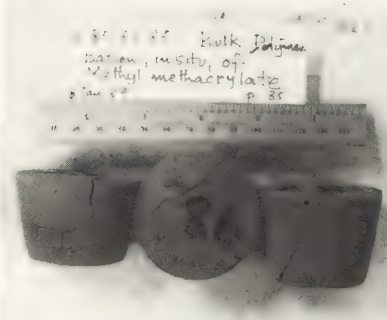


Fig. 11 Low temperature bulk PMMA polymerization.

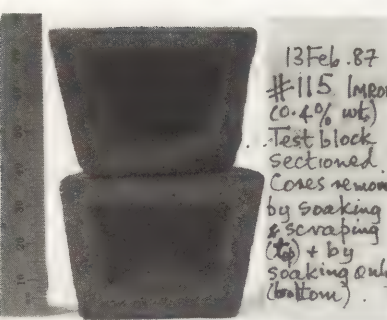


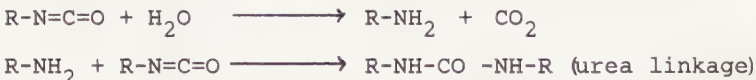
Fig. 12 One half has been soaked in water, the other half soaked and excavated.

perhaps be aware of the possibility of differential separation since long-term consequences are not known. (It should be easy to determine whether separation occurs on powdered sample - stone or adobe - in a chromatography column under a dry atmosphere.)

PMMA, generated in situ by a variation of the elegant precipitation polymerization from n-heptane of Phillips [10] produced extremely resistant blocks (Fig. 10). The technique has drawbacks, however. The outer thin layer was poorly consolidated and disintegrated in the first cycle. Also, the difficulty in obtaining low temperature di-alkylperoxocarbonate initiators and their somewhat erratic polymerization behaviours makes the system a difficult one. Nonetheless, it is worth persevering with because of the inexpensiveness and availability of the monomer and the proven characteristics of the polymer. Other attempts at precipitation polymerization from n-heptane with other initiators (benzoyl peroxide, lauroyl peroxide, methylethylketone peroxide) and tertiary amine promoters (NN-dimethyl-p-toluidine) were unsuccessful, possibly due to absorption or neutralization of the amine by clay minerals. Bulk low temperature polymerization of MMA in test blocks caused massive cracking (Fig. 11), confirming Lewin's finding [11].

The epoxy system [12], an ultra-low viscosity one used for embedding specimens for sectioning, would appear to have no application in adobe preservation.

Undoubtedly, the most impressive system was a polyisocyanate based on a prepolymer of HDI. Test blocks cured to a tough, hard finish with a stone-like ring, and without color change. Polymer loading in the matrix was low (0.3-1.3% by weight). No deterioration or cracking occurred on testing; even the surface coated blocks with a layer only 1-2mm thick repeatedly absorbed 13% w/w of water. It performed well in water-transmission experiments and resistance to salt crystallization (Tables 6,7). An important finding in surface coated blocks was that no abscission layer occurs at the boundary. In sectioned blocks there is clear evidence of graded consolidation (Fig. 12). We interpret this, on our present understanding of the system, as being due to chromatographic separation of prepolymer by molecular weight during infiltration followed by evaporation of solvent and reaction of isocyanate end-groups with water from the atmosphere and in the clay matrix:

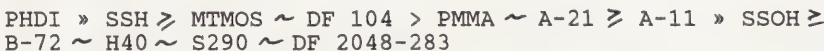


Polymers based on PHDI show good light and environmental stability [13] but are expensive. In our laboratory work no attention was paid to cost in the search for the best materials. The claim that so-called hi-tech materials are too expensive and therefore not worth investigating for conservation use is in our view not always tenable. It is worth quoting from a recent editorial [14] "there is a need for research in historic materials science. The prerequisite is a clear specification of the properties required; the next step is to develop the materials, followed by the third stage: commercialization at a price allowing practical service."

There is a vast field of chemistry, loosely called polyurethane chemistry, based on the organo-isocyanates, R-N-C=O. This potential for tailoring systems for specific applications has hardly been explored by conservation scientists. In the field of adobe the little work reported on polyurethanes to date [15], [16], [17] has been ill-defined in terms of composition of the materials. It is known that the work of Abdurazakov in Uzbekistan used a polyurethane based on a di-isocyanate, but details of the type and co-reactants, if any, are not given. Results and durability of the material are stated [15] to be excellent.

CONCLUSIONS AND FUTURE WORK

The test methods developed afford a means of qualitatively rank-ordering preservatives as a preliminary to more detailed laboratory examination and field evaluation. Adobe test blocks prepared in this way may also find wider use as a screening model in stone conservation where structural and chemical inhomogeneity is sometimes a problem. Our results give an approximate order of effectiveness, in terms of the three tests, for adobe preservation:



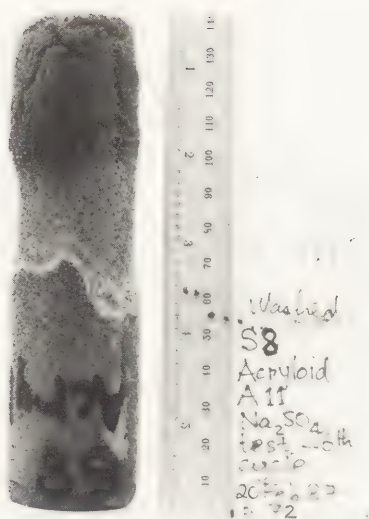


Fig. 13 Acryloid A-11 after sixth cycle, washed to reveal the extent of fretting.

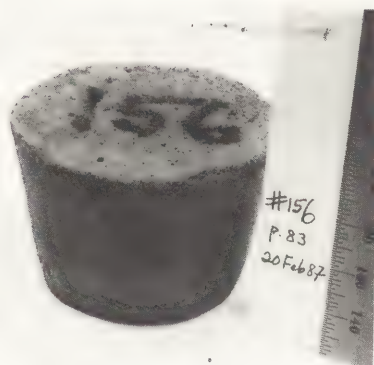


Fig. 14 PHDI (0.3% polymer loading), after three wet/dry cycles.

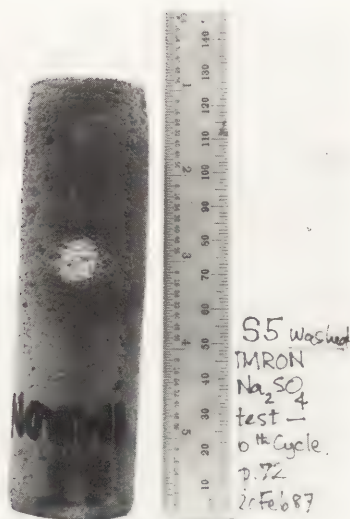


Fig. 15 PHDI (0.8% polymer loading) after six salt cycles.

Taking into account factors such as the undesirability of high hydrophobicity we would exclude DF 104 and regard all the systems from PHDI to A-11 as being worth more detailed investigation. The two good Acryloids were less successful than the others in resisting sodium sulphate (Fig. 13).

The best all-round performance was delivered by the polyisocyanate (Figs. 14,15). So impressive were its characteristics that we feel confident that it, and related systems such as the methylenedicyclohexyl analogue, both with well established resistance to outdoor degradation, will find applications in the field and indeed in stone conservation too. The combination of wet strength, resistance to salt crystallization, and water transmission at low polymer loading could be useful in desalination of deteriorated stone. A caveat would be in order at this point: we are not suggesting immediate application but are urging evaluation on other substrates and by other test procedures. Reversibility and freeze-thaw resistance have to be investigated, as has the mechanism of protection. Methods for introducing infiltrants thoroughly and uniformly into bulky structures have also to be developed and, while we have results on a scale wall using a gravity feed system, refinements and further work are needed.

Outdoor heritage sites have individual characteristics in terms of location, material composition, climate and so on. Ideally, to solve the preservation needs of a site requires detailed analysis followed by selection of appropriate measures and techniques from a range, a "menu", of options. In the difficult area of adobe preservation the options are often non-existent. We have identified several areas in need of research: chemical preservatives and consolidants; materials and design for site shelters (since no single chemical treatment is ever likely to provide a panacea for adobe); measures for ground water control; development of a quantitative erosion/weathering model. As previously stated, we see these as goals achievable through a combination of laboratory and field work. For example, the photogrammetric documentation of Fort Selden since 1974 can provide a base for quantitative modeling of erosion; while the availability of the adjacent test site for evaluation of test walls, with trained staff on hand to record environmental conditions and monitor deterioration is unparalleled.

Finally, it is our thesis that adobe, the oldest of man-made composites, can be modified to improve its durability with minimal chemical intervention by using state of the art materials. These, coupled with results of shelter and drainage control work hold out the prospect of a whole-site preservation synthesis.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Charles Selwitz and Dr. Frank Lambert for their valuable suggestions, discussions and help in obtaining materials. Dr. Robert Graham kindly provided and delivered the initiator di-isopropyl peroxocarbonate, and David R. Stuart of San Buenaventura provided the raw adobe. We also wish to thank Mary Riedel for her help in preparing the manuscript.

REFERENCES

1. Exodus 5, 7-12.
2. Gordon, J.E., The New Science of Strong Materials, 2nd edition, Penguin Books (1976).
3. Among the oldest extant remains are those in Turkey (9000BP), Mellaart, J., Scientific American 210 (1964): 94; the Canaanite triple-arched gate at Tel Dan, Israel (3800BP), Biran, A., Israel Exploration Journal 34 (1984): 1; Mohenjo-Daro in the Indus Valley, Jansen, M., Endeavour, New Series, 9 (1985): 161; and the still inhabited Acoma Pueblo in New Mexico.
4. Dethier, J., Unesco Courier, March (1985): 31-33.
5. Spry, A.H., "Chemical Preservation of Sydney Sandstone," Report No. 1458 of The Australian Mineral Development Laboratories, Flemington Street, Frewville, So. Australia 5063 (1983): 10.
6. Clifton, J.R., Brown, P.W. and Robbins, C.R., National Bureau of Standards, Technical Note 977 (Washington D.C., 1978).

7. Phillips, M.W., "Acrylic Precipitation Consolidants," IIC Preprints, Washington Congress (1982), p. 56.

8. Vassallo, J.C. and Lewin, S.Z., Preprints of the Contributions to the International Symposium, Bologna (1981): 587.

9. Munnikendam, R., ICOMOS, Yazd, Iran, 1972. Proceedings published by UNESCO (1976): 29.

10. Brydson, J.A., Plastics Materials, 3rd edition. Newnes-Butterworth, London (1975): 633.

11. Editorial: "The Science of Cultural Materials," European Cultural Heritage Newsletter on Research 1 (1987): 3.

12. Abdurazakov, A.A., "Conservation Experience of Clay Construction in Uzbekistan," ICCROM Conference, Ghent, (1985): 81.

13. Pencapsula polyurethane resin at 90% solids in mineral spirits. Texas Refinery Corp., Albuquerque, New Mexico. In unpublished report: Fenn, D.B., Deck, J.R., Herriman, W.P., and Vincent, J.R., "Chemical Stabilization Methods Research at Chaco Canyon National Monument and Bent's Old Fort National Historic Site."

14. Kubicki, K., Maidl, B. and Stein, D., listed in: International Conference: In Situ Soil and Rock Reinforcement, Paris, 9-11 October (1984).

* * *

NOTE: Due to space limitations only Tables 2 and 4 are reproduced here. Tables 1,3,5,6 and 7 are available from the authors here at the meeting or by writing to Neville Agnew, Queensland Museum or James Druzik, The Getty Conservation Institute.

Table 2 - Erosion Ratings - Test Walls

After 12 months exposure:

Very little erosion = 5
Little erosion = 4
Moderate erosion = 3
Serious erosion = 2
Very serious erosion = 1

#	Treatment	Wall Direction				Avg.
		N	S	E	W	
1	Control without straw	2.5	3.5	3.5	2	2.9
2	El Rey Superior 200	5	5	5	4.5	4.9
3	Daraweld-C	4	5	5	5	4.8
4	Asphalt emulsion	5	5	5	4.5	4.9
5	Superquickseal/Acryl 60	4	4.5	4	4	4.1
6	K & E Mineral Sealer	2	2.5	3.5	2	2.0
7	Linseed Oil	2	2.5	3	1.5	2.3
8	Thorocoat	5	5	3	5	4.5
9	Agave juice extract*	3.5	3.5	2.5	3	3.1
10	Soil Seal Concentrate	4	4.5	4	4	4.1
11	Silicote	4	3.5	2	3.5	3.3
12	Seal-Krete	2.5	3	3.5	1	2.0
13	Control with straw	3.5	3.5	3	2.5	3.1
	Severity of exposure direction	47.0	51.0	47.0	42.5	
	Averages	3.6	3.9	3.6	3.3	

* After 8 months exposure.

Table 4 - Chemical Systems - Test Blocks

	Product	Supplier/Mfgr.	Chem. Comp.
B-72	Acryloid (=Paraloid) B-72	Rohm & Haas Co.	Acrylic copolymer
A-11	Acryloid A-11	Rohm & Haas Co.	Acrylic copolymer
A-21	Acryloid A-21	Rohm & Haas Co.	Acrylic copolymer
PMMA	Poly (methylemeth- acrylate)	J.T. Baker Chemical Co.	Monomer stabilised with 10ppm MEHQ
MTMOS	Methyl trimethoxysilane	Dow Chemical, Z-6070	
SSOH	Stone Strengthener	ProSoCo, Inc., Kansas City/Wacker Chemie	75% tetra ethyl ortho- silicate + methyl triethoxy- silane in solvents
290S	290 Siloxane	ProSoCo., Inc., Kansas City/Wacker Chemie	6.7% Oligomeric siloxane with long alkyl groups in ketones
H40	H40 Water Repellent	ProSoCo., Inc., Kansas City/Wacker Chemie	40% low molecular weight silicone resin in solvent
DF 104	Dri Film 104	General Electric Co.	70% silicone resin in aromatic solvent
DF 1048- 283	Dri Film 1048-283	General Electric Co.	Silicone resin in mineral spirits
PHDI	Imron Activator 192S	E.J. Du Pont de Nemours & Co.	Prepolymer of hexameth- ylene-1,6- diisocya- nate in ester sol- vents
Epoxy	Ultra-Low Viscosity Embedding Medium	Polysciences, Inc.	Vinyl cyc- lohexane dioxide with hardener, modifier and catalyst

SUMMARY

It was noticed that the Taj Mahal marble was getting discoloured acquiring a yellowish appearance. It was feared that the discolouration was due to the effect of atmospheric pollution. Studies conducted at the NRLC indicate that the yellowing was due to several other causes but not due to pollution. The presence of an acrylic resin on the surface of marble in several areas was detected. This could also have been one of the causes of yellowing.

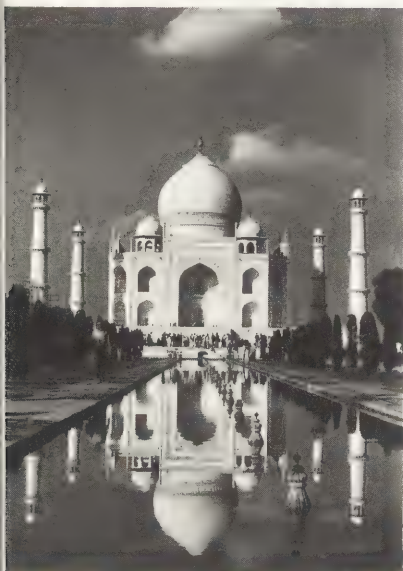


Fig.1 Taj Mahal

DISCOLOURATION OF TAJ MAHAL MARBLE - A CASE STUDY

O.P. Agrawal, Tej Singh, B.V. Kharbade, Kamal K. Jain and G.P. Joshi
National Research Laboratory for Conservation of Cultural Property
E/3, Aliganj Scheme, Lucknow-226020 (India)

INTRODUCTION

The Taj Mahal, an architectural marvel, is considered to be one of the most beautiful monuments of the world (Figure 1). It is a brick masonry structure having a white marble veneer inlaid with coloured stones. The preservation of the monument has been a matter of great concern for quite some time. This concern became manifold after the setting up of an Oil Refinery at Mathura, about 40 Km. away from Agra because it was feared that the pollution due to the Mathura Refinery would have a serious adverse effect on the marble of the Taj Mahal. In fact, the yellowing of the appearance of the Taj Mahal marble was ascribed by several scientists to the changes due to the pollutants emitted by the Mathura Refinery [1]. The cracks in the marble slabs fitted on the walls of the monument were also seen as a result of the effect of pollution. Reports have been appearing in the newspapers about the danger to the Taj Mahal because of these various factors. A fear was expressed by some scientists that Taj Mahal was suffering from 'stone cancer', whatever that term might mean. Statements to the effect that Taj Mahal was deteriorating fast were given by scientists and non-scientists, politicians and others, expressing their concern about the safety of the Taj Mahal, and probably rightly so, because this great monument does represent the finest period of India's architectural history. In spite of all this concern, there have not been many serious scientific studies on the nature of the deterioration of the Taj Mahal materials. Probably the first serious study was by Marissa Tabasso and other experts on behalf of Techneco of Italy. Most studies mainly related with the impact of pollutants on the materials of the Taj Mahal [2,3,4,5,6,7,8] and the characterization of marble, mortar and plaster samples from the Taj Mahal [8,9].

During our visits to the Taj Mahal, we observed that the Taj Mahal marble had discolouration of various types. Surface samples from several of these areas were collected and studied, and the results of the examination of the samples along with the explanation of different types of discolouration are described in this paper. It is hoped that the studies will provide a basis for systematic conservation of the monument.

NATURE OF DISCOLOURATION

The marble slabs used for the Taj Mahal are white. However, all of them are not perfectly white. Some of them have spots, or streaks of different natural colours produced because of mineral impurities. It was being noted for some time that the white marble surface of the monument was getting discoloured. What was of a great concern was the appearance of a yellowish layer all over the white marble, particularly in the niches and arches. Besides this, there were several types of discolourations in different parts of the monument.

Discolouration of the marble surface has taken several forms. These are:

- i) Uniform yellowing of the surface particularly inside the niches and the arches.
- ii) Blackish accretions on the cenotaph and on the walls of the gallery inside the monument.
- iii) Yellow-grey deposits on the brackets used on minarets.
- iv) Brown rust-like stains.
- v) Brown spots.
- vi) Green-black deposits.
- vii) Black patches.

GENERAL YELLOWING OF MARBLE SURFACE INSIDE NICHES

It was observed that the walls of the large arches (niches) have acquired a general yellowish appearance, particularly their upper portions. The parts of niches which receive rain water splashes appeared cleaner. On the other hand, the upper portions which do not receive rain water splashes are rarely clean. As a result, dirt and cobwebs had deposited imparting to the marble surface a dirty yellowish appearance. Similar accumulations were present in other areas of the monument which are protected from the rain, e.g. the inner portions of the monument.

It was also noticed that although the lower portions of the niches on the outer side of the monument receive splashes of rain water, the marble slabs have become dirty yellowish. Samples of this yellowish dirty accretions were collected from several places and tested for presence of sulphates by micro-chemical techniques and colorimetrically. In none of the samples, any sulphate could be detected. It would be safe to conclude that the yellowing of the marble is not due to the effect of pollution.

X-ray diffraction patterns indicated only the presence of calcite (coming from marble) and clay minerals due to dust particles.

We then wanted to ascertain if the yellowish appearance could be because of any type of organic coating that might have been applied to the monument in the past. To test this possibility, attempt was made to take the samples with the help of cotton swabs using various solvents and mixtures of solvents, like:

- i) Toluene
- ii) Xylene
- iii) Mixture of toluene and xylene
- iv) Trichloroethylene
- v) Mixture of trichloroethylene and toluene
- vi) Mixture of trichloroethylene, toluene and xylene.

Out of these, toluene was found to be the most suitable. Samples were taken from several different parts of the monument. The extracts of the swabs were analysed by infra-red spectrometry using specular reflectance technique. Apart from recording the infra-red spectra of the samples collected from the surface of the Taj Mahal, reference spectra of polymerised methylmethacrylate, solution of 'perspex' sheet (a polymethylmethacrylate preparation), polyvinyl acetate, paraffin wax, and some other resins available in the Laboratory were prepared. Simultaneously, a control spectrum of the extract of only cotton swab in toluene was also taken. The spectra recorded are given in Figures 2-7.

It was seen that infra-red spectra of the samples from the Taj Mahal matched exactly with the spectra of polymethylmethacrylate or the solution of 'perspex' sheet which is also an acrylic resin. Samples were taken from 35 spots from different areas, out of which 20 gave positive results for the presence of an acrylic resin.

It was thus apparent that the general yellowish appearance on outside the marble surface was because of the change in the transparency of the polymethylmethacrylate or some other acrylic resin coating which was applied on the surface of the Taj Mahal at some point of time. It is known that polymethylmethacrylate and other acrylic resins change from transparent to yellow colour in course of time, depending on their nature and composition [10], particularly when the material used is not of the purest quality.

Solutions of polymethylmethacrylate (or 'perspex' scrapings) and of polyvinyl acetate are the two most common protective coatings used in India for the preservation of monuments [11, 12]. Polymethylmethacrylate solution when applied fresh is transparent but with time it acquires a yellowish colour. Probably it does not matter much when the application is on coloured stones like sandstone or granite, but on the white marble surface it will cause a change in its appearance giving it a slightly yellowish tone. This also explains the uniformity of the yellowish appearance of the surface.

This finding leads to a very important conclusion that a protective coating should not be applied on any surface, even stone, unless its properties have been fully tested.

We have also seen that for the removal of these aged products, a mixture of acetone plus cyclohexane and toluene, can be used very satisfactorily.

We are now conducting experiments on other Indian monuments as well, to determine whether the yellowish appearance in some other marble monuments is also because of the change in the colour of the protective coatings given at some time, or because of some other reason.

BLACKISH ACCRETIONS ON THE CENOTAPH AND ON SOME OF THE WALLS OF THE INSIDE GALLERY

A rather thick layer of blackish accretions was present on the lower portions of the walls of the corridor inside the monument, on the cenotaph and on some other areas which are constantly touched by visitors.

In order to determine the nature of these accretions, we tried several analytical techniques. This accretion is insoluble in water. With organic solvents, it gets completely dispersed leaving behind a powdery residue. On ignition, the black accretion ignited easily leaving small amounts of similar powdery residue.

On the basis of these preliminary tests, it could be surmised that the accretion mainly consisted of palm grease with accumulated dirt.

YELLOWING/BLACKENING OF BRACKETS ON MINARETS

The brackets used for supporting the balcony of minarets are largely protected from direct rain. These brackets had also yellowed in general and the areas totally protected from rain had blackened.

A piece of bracket replaced some time ago from the first floor of the S-W minaret was obtained from the stores for experimentation. The piece was having a uniform blackish deposit in some areas and the rest of the exposed area was yellowish. This blackish layer could be chipped off easily with the help of a sharp knife. It was observed that only the outer side of the chips thus removed was black. The inner side was white.

The chipped off sample was analysed by X-ray diffraction and ignition test. The sample did not burn off on ignition but turned reddish in colour. Qualitative analysis

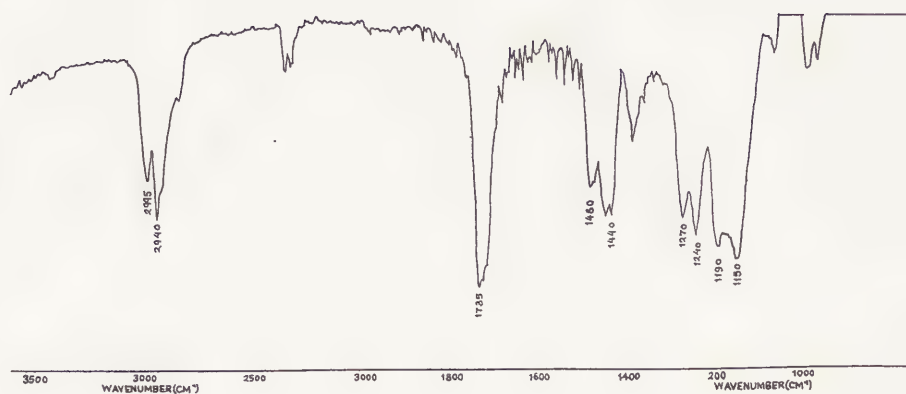


Fig.2 IR spectra of polymethylmethacrylate (polymerised from monomer)

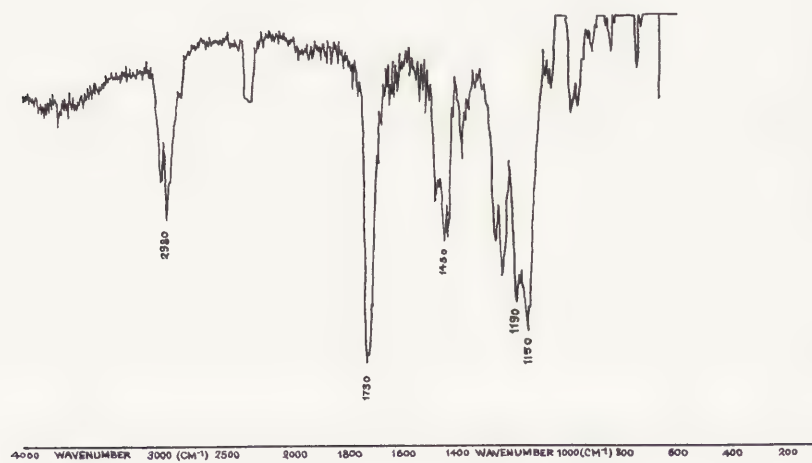


Fig.3 IR spectra of 'perspex'

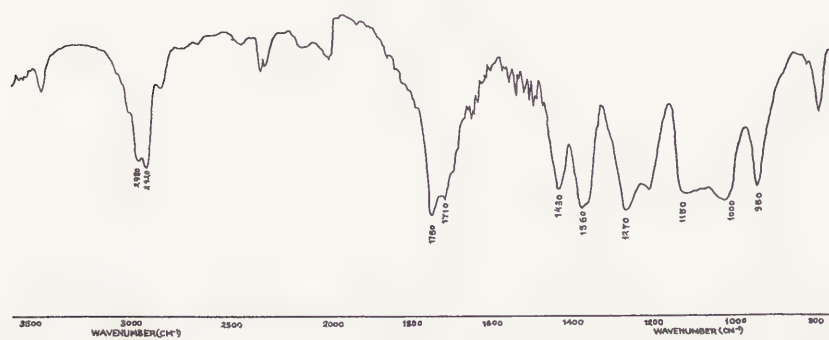


Fig.4 IR spectra of polyvinyl acetate

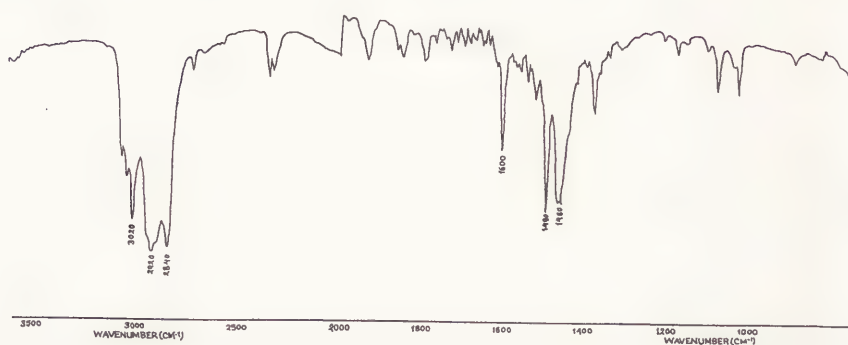


Fig.5 IR spectra of paraffin wax

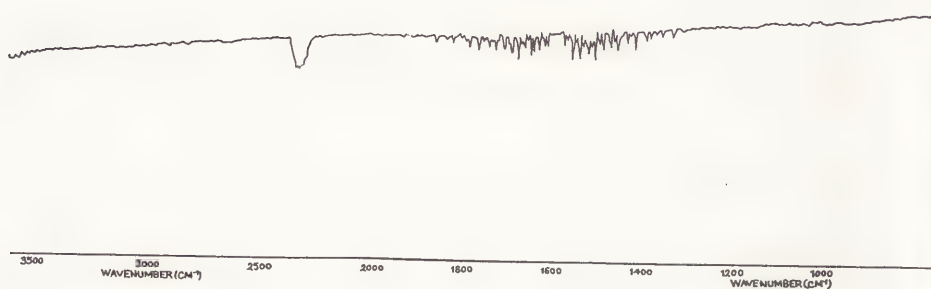


Fig.6 IR spectra of the extract of cotton swab in toluene

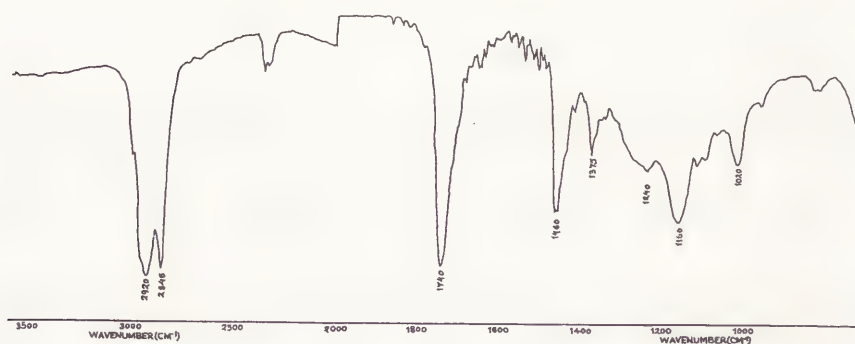


Fig.7 IR spectra of a representative sample taken from Taj Mahal



Fig.8 Brown stain due to rusting of iron dowel



Fig.9 Mosquitoes leave green black excreta on the white marble surface

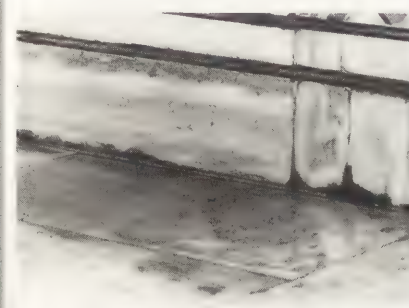


Fig.10 Algae grow on surfaces which remain wet for longer period

by emission spectrography confirmed the presence of aluminium, silicon and iron. This shows that the dirt is soil dust. X-ray diffraction studies on the chipped off sample were done by using Debye Scherrer camera of 114.5 mm diameter and Cu-K α radiations. The d and I/I_0 values for the diffraction pattern obtained are given in Table 1. On comparison of the d and I/I_0 values with the JCPDS standard values, it was found that the chipped off sample mainly consisted of weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) with small amounts of whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and traces of calcite (CaCO_3) and quartz (SiO_2). In India, it is a common practice to clean modern masonry with oxalic acid. Formation of calcium oxalate suggests that the Taj Mahal marble had been cleaned with ammonium oxalate or oxalic acid in the past, at least in some parts, and the excess reagent was not washed off thoroughly which led to the formation of calcium oxalate on the surface. Molecular size of calcium oxalate being higher than that of calcite, it formed a crust on the surface of marble allowing deposition of dirt from suspended particulate matter in the air. The areas exposed to rain got cleaned by repeated washing by water each year during monsoon but the areas protected from rain retained accumulations of dirt.

BROWN STAINS DUE TO RUSTED IRON DOWELS/CLAMPS

Iron dowels and clamps had been used for joining marble slabs to one another. At a few places on the mausoleum, iron dowels/clamps were found to be exposed due to bursting of marble. The iron dowels/clamps exposed to rain have further corroded and the rust stains flow down the marble surface and disfigures the marble. Such stains were found on two columns, one on the north and the other on the west direction (Figure 8).

BROWN SPOTS DUE TO IRON MINERALS PRESENT IN THE MARBLE

Marble always contains some mineral impurities. Mineral impurities present on the stone surface may undergo chemical changes due to the action of moisture and the atmospheric oxygen. Thus, the iron minerals present in marble are converted to iron salts giving rise to brown spots on atmospheric oxidation. These types of spots are visible on the Taj Mahal marble also at several places.

Since these spots are inside the stone, and are a part of the stone structure, it is difficult to clean them without affecting the stone. In fact, it is not necessary to clean them, because they are not harming the stone in any manner.

DISCOLOURATION DUE TO MOSQUITO EXCRETA

At the Taj, a very unexpected cause of formation of black spots was observed, and this was the dense deposit of mosquitoes excreta on the marble surface (Figure 9). The cool northern side of the monument facing river Yamuna is apparently a very good resting place for mosquitoes particularly during summers. It seems that the stagnating water on the bank of the river forms a good breeding ground for mosquitoes and during summers, swarms of mosquitoes rested on the lower northern portions of the monument. Their excreta formed a greenish accretion on the marble. The control of mosquitoes is mostly a question of cleaning the surroundings and taking steps to avoid stagnation of water around the monument. The excreta could be washed away with ordinary water during regular maintenance of the monument.

BLACKISH PATCHES DUE TO ALGAL GROWTH

In some areas of the monument, there are black spots which can be attributed to the algal growth. This type of discolouration however, is limited only to some areas, particularly those which remain wet for longer periods, for instance the area directly under water-spouts. Also at the periphery of the base of the mausoleum and on the sides of the outside niches, rain water remains accumulated for considerably longer periods during monsoons. At these places algal growth was found, resulting in a black incrustation (Figure 10).

ACKNOWLEDGEMENT

Thanks are due to Shri Anil Risal Singh, Sr. Photographer for the photographs.

REFERENCES

1. Rohatgi, P.K., Raju, C.B., Ray, A.K., Modi, O.P. and Rao, U.M., Materials damage and research imperatives at Taj Mahal, A report submitted to the Government of India (1984).
2. Studies for the preservation of monuments in Agra from Mathura Refinery air pollution, Third Report, TECHNECO, Italy (1976).
3. Report of Expert Committee on Environmental Impact of Mathura Refinery, Chairman: Dr.S. Varadarajan, (1977).
4. Dave, J.M., Key note address, National Seminar on Effect of Atmospheric Pollutants on Monuments, Lucknow, (1986).
5. Report on 'Air Pollutants Effect on Historical Monuments', submitted to the Department of Environment by Shriram Institute for Industrial Research, Delhi (1985).

6. Ganorkar, M.C. and Reddy, M.B., Studies on pollution profile of Taj Mahal, National Seminar on Effect of Atmospheric Pollutants on Monuments, Lucknow, (1986).
7. Lal, B.B., Taj Mahal - Some problems of environmental monitoring and weathering studies, Rome Conference (1984).
8. Tandon, B.N., Comprehensive researches on the effect of weathering, pollutants e.g. SO_2 and particulates on the marble of Taj at Agra, A Report submitted to the Archaeological Survey of India (1985).
9. Aslam, M., Characterization of ancient mortar and plaster, A Report submitted to ICCROM, Rome (1986).
10. Shields, J., Adhesives Handbook, New-Butterworths, London (1979), p.34.
11. Tandon, B.N., Stone in Indian monuments and other art objects - problems in its conservation, Conservation of Cultural Property in India, 13, 17 (1980).
12. Subbaraman, S., Conservation of stone temple, Mahabalipuram and Kailash Nath temple, Kancheepuram, Proc. 5th Intl. Congress on Deterioration and Conservation of Stone, Lausanne (1985), Vol.II, p.1027.

Table I : X-ray diffraction data of blackish accretion present on a first floor bracket of S-W minaret.

Line No.	Sample		Standard Value		Mineral
	d	1/10*	d	1/10**	
1.	6.23	100	6.18	100	Weddellite [±]
2.	5.87	10	5.93	100	Whewellite ^{±±}
3.	4.45	20	4.42	30	Weddellite
4.	3.93	5	3.91	8	Weddellite
5.	3.65	10	3.65	70	Whewellite
6.	3.35	10	3.343	100	Quartz ⁺
7.	3.04	5	3.035	100	Calcite ⁺⁺
8.	2.78	80	2.775	65	Weddellite
9.	2.49	5	2.495	14	Calcite
10.	2.42	5	2.42	8	Weddellite
11.	2.36	10	2.355	30	Whewellite
12.	2.24	10	2.243	25	Weddellite
13.	2.13	5	2.12	8	Weddellite
14.	2.09	5	2.08	14	Whewellite
15.	2.03	5	2.024	6	Weddellite
16.	1.96	10	1.957	10	Weddellite
17.	1.90	10	1.899	16	Weddellite
18.	1.84	5	1.836	10	Weddellite
19.	1.74	5	1.741	6	Weddellite

* Estimation by visual observation.

** Measurement by Photometer.

± JCPDS Powder Diffraction Data for Minerals 17-541.

±± JCPDS Powder Diffraction Data for Minerals 20-231.

+ JCPDS Powder Diffraction Data for Minerals 5-490.

++ JCPDS Powder Diffraction Data for Minerals 5-586.

SUMMARY

Marble veneer of the Taj Mahal shows signs of physical weathering in the form of cracking, chipping and bulging of marble slabs which have been caused mainly by the stresses due to the load on the marble slabs. Stresses due to swelling of iron dowels, jerks received during quarrying etc. also play an important role. Chemical action of rain water is also contributing towards deterioration by preferentially leaching out mineral impurities.

STUDY ON THE WEATHERING OF TAJ MAHAL MARBLE

O.P. Agrawal, Tej Singh and Kamal K. Jain
National Research Laboratory for Conservation of Cultural Property
Sector E/3, Aliganj Scheme
Lucknow-226020 (India)

1. INTRODUCTION

Taj Mahal a massive brick masonry work veneered with white marble, was built in the mid 17th century. The monument stands on the southern bank of river Yamuna on a 6.7 m high square platform having side dimensions of 95.4 m. The main mausoleum is also square in shape with 57.0 m sides. The top of the mausoleum is a double dome structure with a metal pinnacle. The total height of the monument above the garden level is 74.4 m. There are four minarets of 46.2 m height, one on each corner of the platform.

Over the years, the marble of the Taj has started showing signs of deteriorations. Apart from discolouration of the surface, which has been dealt with in a separate paper, cracks had formed in marble slabs, there was pitting in some areas. There were other defects as well. It was remarked by several persons that all the changes in the marble were due to pollution. However, according to us, it needed a serious study before any conclusions could be drawn. This paper describes in detail the results of our studies on the nature and causes of different types of deterioration observed on the Taj Mahal marble veneer.

2. TYPES OF DETERIORATION

With an aim to identify the types of deterioration of the Taj Marble, the Taj was visited several times for visual observation, collection of samples and photographic documentation of the observed signs of deterioration. The types of deteriorations observed on the Taj Mahal are as follows :

- i) Formation of cracks in marble
- ii) Chipping and breaking of marble slab edges
- iii) Bulging of marble slabs
- iv) Pitting or erosion of marble surface, only in some areas.

3. FORMATION OF CRACKS

Cracks of varying nature and magnitude are seen on the Taj Mahal marble veneer. Though most of them appear to be superficial, some of them are quite deep and in some cases they are extending beyond one slab. Cracks on minarets are fewer than on the mausoleum.

Formation of cracks could be attributed to the following possible factors :

- Inherent defects in the stone developed due to residual stress at the time of quarrying, trimming, etc.
- Effect of the load due to marble slabs placed one over the other.
- Shift in the foundation level.
- Chemical weathering due to rain water.
- Insolation weathering.

It is possible that all these factors were simultaneously playing a role in the formation of cracks. We shall present here our observations on the causes of formation of cracks of various types.

3.1 Vertical Cracks

There are hairline cracks present in some parts of the monument. Most of the cracks developed on marble veneer are along the vertical plane and the majority of them appear to be superficial.

There was a suggestion that cracks in marble have formed due to thermal changes. The surface temperature of marble exposed to direct sun reaches up to 50°C during summers and during winters it may be as low as 5°C. Besides, there is a different of temperature between day and night which sets a daily temperature variation of nearly 20-25°C.

On heating, calcite of marble expands 2% parallel to the c-axis but on cooling contracts 0.5% perpendicular to it. This type of expansion and contraction of calcite in crystallographically-oriented marble may lead to decay of the stone [1]. However, a temperature cycle of 20°C alone may not be so important towards the formation of cracks. Had this been so, cracks would have appeared equally in horizontal, vertical and other directions. Moreover, vertical cracks are also present in areas which do not receive direct sunlight. Therefore, the effect of temperature in producing vertical cracks appears to be minimal.

When a rock is under compressive stress, it may fail by induced brittle fracture



Fig. 1 The marble slab just below the column on left side has broken due to load concentrated at the point

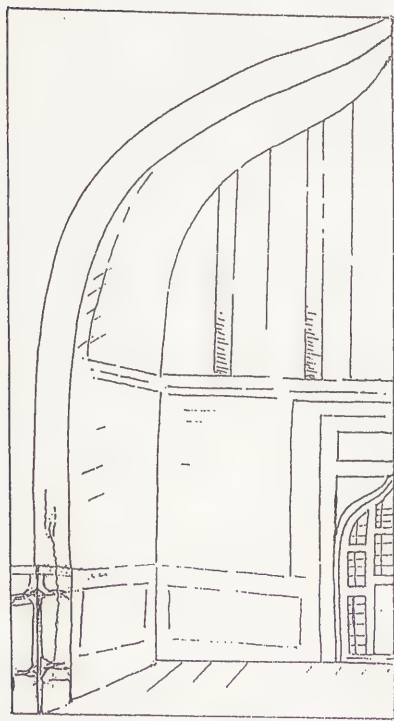


Fig. 2 Sketch of an arch of the central hall showing vertical cracks on the base of the arch



Fig. 3 Cracks along the veins of mineral impurities present in marble

and cracks will develop parallel to the direction of stress [2]. Therefore, these vertical cracks could at least partly be attributed to the downward pressure exerted by the load of marble slabs on the lower slabs. The stress due to expansion of the outer surface of the slabs because of the action of heat from the sun could be having a synergistic effect.

We observed that the slabs just under the columns on the sides of the outer niches have been broken (Fig. 1). Furthermore, very deep vertical cracks extending to more than one slab in length are noticed at the base of the arches in the central hall (Fig. 2). These cracks on both sides of arches are almost at the same height from the floor. The temperature of slabs in the central hall does not change much during diurnal cycle, therefore, the heat effect can be regarded as absent. Thus, in our opinion, concentrated load due to the arches on their bases appears to be the main reason for the formation of these vertical cracks. The same may be true for the formation of vertical cracks on other parts of the monument where downward pressure is exerted by the load of the slabs.

When we examined the dome, a similar phenomenon was observed. The slabs in the upper part of the dome do not have many cracks, while the slabs in the lower part i.e. the drum, are having extensive vertical cracks.

Furthermore, the marble slabs fitted on the floors i.e. which do not carry any weight on them, are having very few cracks.

These observations indicated that the load due to thick marble slabs is contributing to the formation of cracks on the lower slabs.

Dowels and mortar used for fixing marble veneer to the brick masonry, is expected to reduce the load of a slab on the lower slabs; but the effect of the load due to marble slabs can be seen in the outer niches where the slabs of the floor lying just below the marble veneer have got depressed. Similarly, the slabs on the terrace floor at the periphery of the mausoleum have also got slight depressions. This indicates that veneer slabs are exerting considerable downward pressure.

3.2 Cracks along mineral grains

Mineral impurities in marble are quite often present as veins, as can be seen on many slabs on the ground floor walls of the terrace (Fig. 3). At several places these mineal impurities have been preferentially dissolved by rain water, leading to the formation of cracks.

3.3 Cracks due to iron dowels/clamps

Iron dowels and clamps have been used on the Taj Mahal to support the marble veneer. Over the centuries these dowels have corroded slowly. X-ray diffraction studies were done on the corrosion product of a dowel from S-W minaret. The mineral maghemite, $\gamma\text{-Fe}_2\text{O}_3$ was identified in the corrosion product. Maghemite has a spinel-like structure with the iron atoms distributed randomly over the tetrahedral and octahedral sites. Therefore, it occupies much larger volume than the metal for the same amount of iron. Thus, the dowels have swelled considerably after corrosion and are exerting pressure on the marble veneer. In several instances, the cracks, particularly at the joints of the slabs, could be attributed to the pressure of a corroded iron dowel underneath.

3.4 Development of cracks near the replaced portions of the marble slab

When a marble slab is deteriorated extensively, it becomes necessary to replace such portions or the whole piece of stone. At some of the places where replacements have been done, cracks were present and many of them were quite wide and deep (Fig. 4). Apparently, these cracks have developed due to the pressure exerted by the replaced stone piece since they have been made to fit too tightly so that the joints are not very obvious.

4. CHIPPING AND BREAKING OF MARBLE SLAB EDGES

In some places it was noticed that the edges of the marble slabs have chipped off and in some others the marble pieces have broken off near the joints of the slabs.

These types of deterioration may be due to a combined effect of chemical and physical weathering.

4.1 Chipping of lower portions of the marble slabs resting on platform

The lower portions of the slabs resting on the platform have chipped off at some points. It has been observed that at these points, water accumulates and the lower edges of the slabs resting there remain wet for a considerably longer period during monsoons. Prolonged action of rain water has weakened these portions and with the downward pressure due to the load of the veneer slabs, the weakened edges have chipped off.

4.2 Chipping off of marble at the horizontal joints of marble veneer

In some places, edges of both the adjacent marble veneer slabs have chipped

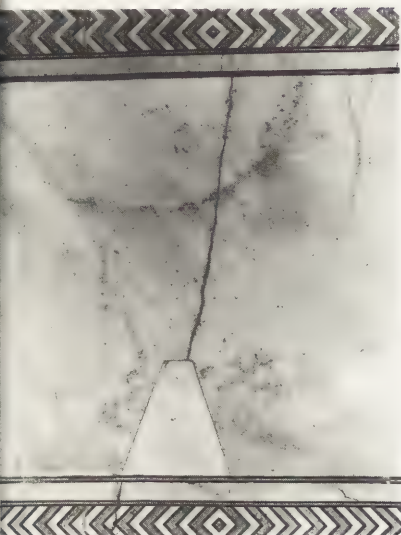


Fig.4 Crack formation adjacent to replaced portion in the marble slab

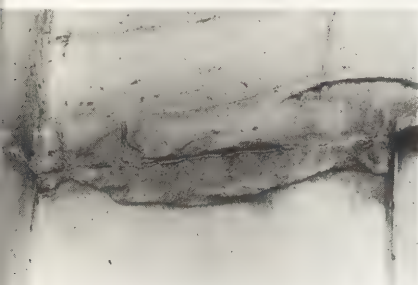


Fig.5 Chipping of marble slab edges at the horizontal joints

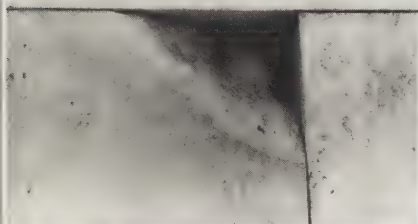


Fig.6 Breaking of marble slab due to rusting of iron dowels

off along the horizontal joints (Fig. 5).

Chipping off of the lower edges of the slabs where chances of water accumulation are there, have been explained to be due to the weakening of the edges of the slabs through the action of water. But the chipping off of the edges of the two adjacent slabs at horizontal joints is present even at much above the floor level and also in places fully protected from rain. Therefore, deterioration due to water can be regarded as minimal. Expansion of slabs due to temperature increase can also be discounted as the cause of stress, since such chipping is present even in the areas fully protected from the Sun, for example, inside the central hall where Sun has no effect.

In this connection, it may be mentioned that jerks received during trimming and subsequent shaping of the slabs make the edges of the slabs particularly weak, and there can be a possibility that the downward pressure exerted due to the load of the slabs results in this type of chipping. This hypothesis is given further credence by the observation that the edges of the two adjacent slabs have chipped off at most of the horizontal joints under the arches in the central hall, which could be due to the fact that at these points the load is much more than on the side walls.

4.3 Breaks due to iron dowels

Iron dowels had been used on the Taj Mahal to join the marble slabs together and to fix them to the brick masonry work. In due course of time on account of the effect of humidity, iron starts rusting and thereby there is an increase in its volume. This exerts a tremendous pressure on the slabs, leading to their breaking at some of the joints. First cracks are produced and then pieces of marble fall off (Fig. 6).

5. BULGING OF SLABS

On visual observation it was noticed that at places some slabs have bulged out and the bulging may damage the slab extensively. We have tried to ascertain the reason for this type of deformation. In our view there are two main possibilities.

5.1 Plastic deformation

A big marble slab on the left side of ground floor south-right outer niche has bulged out in the upper middle portion. This type of plastic deformation can be due to intergranular movement on glide planes or gliding along twinning planes of marble [3]. Deformation due to stress relief could also cause a similar effect. Since splashes of rain water fall on this slab, it may be acting as catalyst in hastening the process.

5.2 Bulging due to iron dowels

At some places on the walls of the central hall, small portions of marble slab edges have bulged out. Such bulgings are very obviously due to swelling of rusted iron dowels. At some places, the bulged out portions have fallen off and the rusted iron dowels are clearly visible.

6. PITTING AND EROSION OF MARBLE SURFACE

On some of the slabs we noticed formation of small pits on the marble surface. Pitting of the marble surface was also ascribed by several persons to the effect of pollution. On close examination we find that this type of deterioration was largely limited only to areas which are directly under water spouts through which water falls on the marble walls (Fig. 7). Obviously, rain water through the spouts flows over the slabs, thereby causing physical and chemical erosion. In the process minerals of the marble are leached out and pitting takes place.

7. CONCLUSION

From the above studies, it is apparent that at present pollution is not playing much role in the weathering of Taj Mahal marble. The marble of the Taj Mahal is still in quite sound condition. It needs to be emphasized that before jumping to conclusions, all aspects of the problem must be taken into account and studied. For each type of alteration there might be several causes. Each one of the them must be considered for precise understanding of the problem.

ACKNOWLEDGEMENTS

Authors will like to thank Dr. Maurizio Marabelli and Mrs. Marissa Tabasso of the Istituto Centrale del Restauro, Rome for useful discussions from time to time. Thanks are due to Mr. Anil Risal Singh, Senior Photographer, NRLC for taking photographs.

REFERENCES

1. Winkler, E.M., *Stone : Properties, durability in man's environment*, Springer-Verlag, Vienna (1975), p.172.

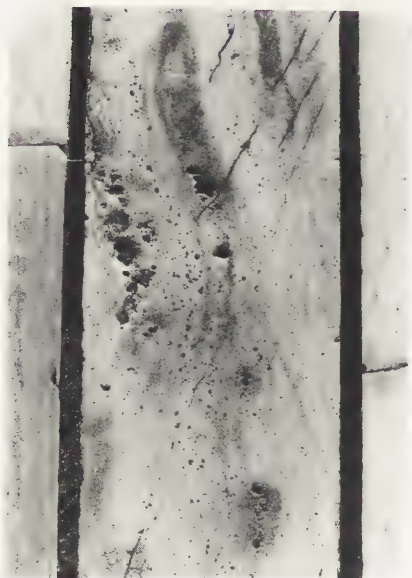


Fig.7 Pitting due to leaching
of mineral impurities with
water

2. Ollier, C., *Weathering*, Longman, London (1984), p.11.
3. *Ibid* 15, p.57.

SUMMARY

The Taj Mahal has been in the news for the last years due to the installation of a huge petroleum refinery in its vicinity. This monument has an internal lining of plaster which has failed due to mechanical causes. Samples of plasters and mortars from these places were studied to assess their state of conservation. From the detailed physico-chemical and instrumental examinations carried out no evidence of active deterioration was found.

STUDIES OF LIME PLASTERS AND MORTARS OF THE TAJ MAHAL

M. Aslam^o, M. Laurenzi Tabasso⁺, P.L. Bianchetti⁺, A.E. Charola[#]

^oCentral Building Research Institute, Roorkee 247 667, India

⁺Istituto Centrale del Restauro, 00184 Roma, Italy

[#]ICCROM, 13 via di San Michele, 00153 Roma, Italy

Introduction

The durability of the Taj Mahal has been in controversy for over a decade due to the commissioning of a six million ton refinery at Mathura, near Agra. The matter has been examined thoroughly and remedial measures are being taken to remove all possible sources of deterioration, including air pollution.

Lime is the most extensively used material in the monument, both for plastering indoors and for mortaring. It has been observed that the plaster work has failed at a few places by cracking, loss of bonding or delamination. While the state of conservation of the stones in the monument (1,2,3) and the environmental pollution around it (3,4,5,6,7) have been a subject of active study during the past few years, not much attention has been paid to investigate its mortars and plasters. Some work has, however, been carried out and is referred to briefly in Indian Archaeology (8). It was thought desirable to carry out a more detailed investigation of the plasters and mortars at the failure places.

Physico-chemical analyses were carried out on both binders and aggregates of the mortars and plasters. Special care was taken in establishing the presence or absence of such alteration products which could result from the effect of acidic atmospheric pollution.

Experimental

1. Sampling and Visual Examination

The sampling of the lime mortar and plaster was done from points on the first floor corridor where the masonry was damaged. Three samples of plaster (TP1, TP2, TP3) and three samples of mortar (TM2, TM3, TM4) were collected.

The samples were examined for their colour, the nature of the aggregate, the presence of lumps of lime, fibers, etc. The nature of the fine aggregate was observed by removing the coarse aggregate and digesting the rest of the sample in 1:1 HCl and separating the fine aggregate after completion of the reaction. The visual characteristics of these mortars and plasters are given in Table I. Detail of the nature and size of the coarse aggregate is given to Table II.

2. Chemical Analyses

A fairly representative sample of each mortar and plaster was ground finely to pass a 150-micron sieve and dried in an air-circulating oven at $105 \pm 2^\circ\text{C}$ for 18 hours and then stored in a desiccator.

The determination of loss on ignition, acid insoluble residue and alumina were carried out according to ASTM procedures (9). This was complemented with the determination of the concentration of calcium, magnesium, iron; sodium and potassium ions by atomic absorption spectroscopy. The carbonate content was determined by calcimetry (10).

Further chemical analyses were carried out following a simplified system for the characterization of ancient mortars (11,12). The determination of the 1:4 HCl acid insoluble residue, the total silica by the classical flux method and the amount of free lime according to the Leduc method completed the chemical characterization of the samples. The results obtained from all of these analyses are reported in Table III.

With these data, the "mineralogical" composition of the mortars and plasters can be calculated through a three equation system (11,12). This composition is given in Table IV.

The presence of soluble salts was established in the water extract of the samples (500 mg of powdered dry sample in 100 ml of water). The concentration of the different ions was determined by means of an autoanalyser except for sodium, potassium and magnesium ions whose concentration was determined by atomic absorption spectroscopy. The electrical conductance and the pH of the aqueous extracts

Table I - Visual Characteristics of Plasters and Mortars

Sample	TP1	TP2	TP3	TM2	TM3	TM4
Colour:						
exposed	whitish buff	grey	greyish white	-	-	-
unexposed	whitish buff	cream. white	cream. buff	light buff	dark buff	reddish buff
Coarse aggreg.	P	A	A	P	P	P
Fine aggreg. (fine sand)	light brown	grey. buff	light buff	light buff	light brown	light brown
Lumps of lime	P	A	A	P	P	P
Fibers	P(tr)	P	P	A	P(tr)	P(tr)

A= absent; P= present; P(tr)= present in trace quantities

Table II - Type and Size of Coarse Aggregate

Sample	Type	Max. Diam (mm)	Colour
TP1	Calcareous gravel	15	dark brown
	Non-calcareous	10	black
TM2	Calcareous gravel	10	grey
	Siliceous gravel	12	dark brown
	Calcareous gravel	8	black
TM3	Non-calcareous	8	greyish black
	Calcareous gravel	12	dark brown
	Siliceous gravel	12	dark buff
	Marble	10	white
TM4	Calcareous gravel	13	reddish buff
	Calcareous gravel	10	dark buff
	Calcareous gravel	8	black

Table III - Chemical Analysis of Plasters and Mortars (% w/w)

Sample	TP1	TP2	TP3	TM2	TM3	TM4
Loss on ignition	24.35	35.22	25.03	28.15	17.73	16.13
Acid Ins. Residue	38.20	15.25	38.61	31.00	51.63	56.15
Ins. HCl 1:4	38.22	16.25	38.67	31.26	52.12	56.42
SiO ₂ total	33.68	15.14	35.42	26.73	47.19	52.23
CaO	33.20	42.42	31.20	35.20	23.10	21.71
MgO	1.93	2.87	2.17	1.92	2.00	1.82
Fe ₂ O ₃	1.60	0.60	0.58	0.91	2.27	1.91
Al ₂ O ₃	1.98	1.09	1.76	2.49	1.78	1.54
Na ₂ O	0.39	0.29	0.32	1.02	0.39	0.41
K ₂ O	0.96	0.44	0.85	0.98	1.25	1.25
CO ₃ ²⁻	31.48	46.15	31.55	37.31	22.60	20.10
CaO free	0.09	0.10	0.12	0.23	0.17	0.11

Table IV - "Mineralogical" Composition of Plasters and Mortars

Sample	TP1	TP2	TP3	TM2	TM3	TM4
CaCO ₃ (%w/w)	47.78	69.94	47.29	57.53	32.76	28.04
MgCO ₃	4.03	6.00	4.53	4.01	4.18	3.80
Ca(OH) ₂	0.12	0.13	0.16	0.30	0.22	0.14
Quartz	16.42	7.68	22.99	16.68	33.08	37.36
Non-Hydraulic Comp.	21.80	8.60	15.68	15.48	19.04	19.06
Hydraulic Comp.	12.72	6.32	9.20	5.52	9.18	10.68

were also measured. The results obtained are given in Table V. Trace amounts of nitrates were found in two plaster samples (TP2 and TP3) while traces of nitrites were found only in one mortar sample (TM2).

Table V - Aqueous Extract Analysis

Sample	TP1	TP2	TP3	TM2	TM3	TM4
pH	7.7	7.9	7.7	7.0	7.6	7.7
Conductance ($\mu\text{S}/\text{cm}$)	57	110	61	72	55	65
$\text{SO}_4^{=}$ (% w/w)	0.18	0.93	0.49	0.45	0.27	0.18
Cl^- (% w/w)	0.32	0.26	0.19	0.83	0.51	0.46
NH_4^+ (% w/w)	0.03	0.02	0.03	0.03	0.03	0.02
Ca^{++} (% w/w)	1.25	2.44	1.45	0.79	0.67	1.05
Mg^{++} (% w/w)	0.02	0.24	0.08	0.01	0.01	0.03
Na^+ (% w/w)	0.10	0.06	0.12	0.61	0.17	0.25
K^+ (% w/w)	0.23	0.12	0.26	0.35	0.32	0.39

3. Mineralogical Studies

The mineralogical studies were carried out by x-ray diffraction (XRD), scanning electron microscopy (SEM) and petrography.

Results obtained by XRD of the powdered samples are given in Table VI.

Table VI - X-Ray Diffraction Analysis of Plasters and Mortars

Sample	TP1	TP2	TP3	TM2	TM3	TM4
Calcite	+++	+++	+++	+++	++	+++
Quartz	++	+	++	++	+++	+++
Mica (muscovite)	\pm	\pm	\pm	++	+	+
Feldspar	-	-	-	\pm	-	-

+++ : abundant; ++ : substantial; + : present; \pm : traces; - : absent

SEM studies were carried out on fracture surfaces of the samples. Figure 1 shows a cross-section of a plaster sample (TP1). Figure 2 shows a detail of the interior of another plaster sample (TP2) at higher magnification.

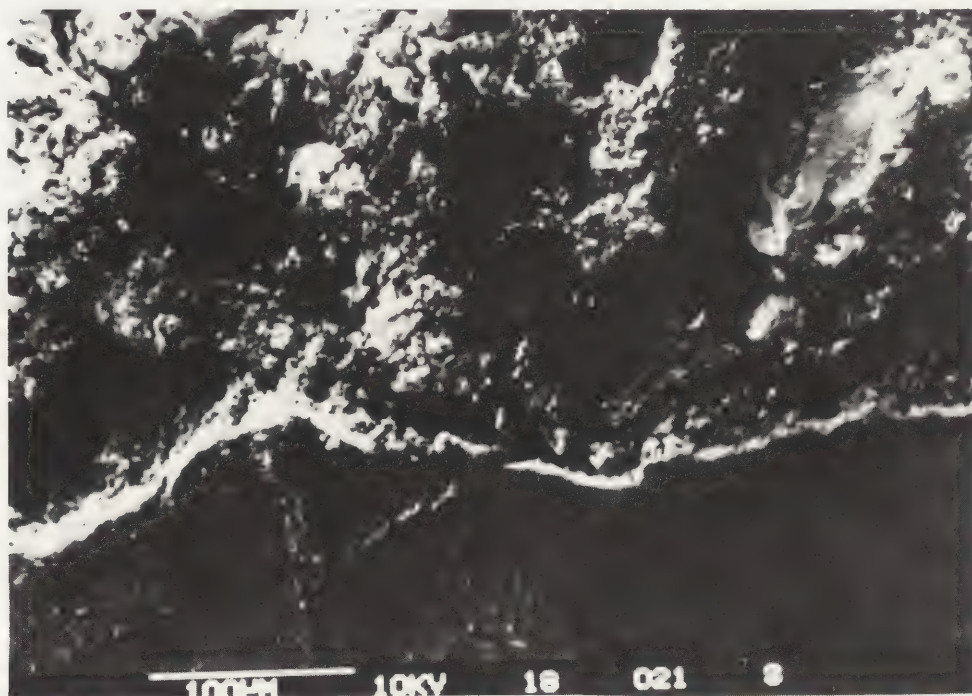


Figure 1. SEM photomicrograph of a cross-section of a plaster sample (TP1) showing the external polishing layer and a view of the internal matrix of the plaster.

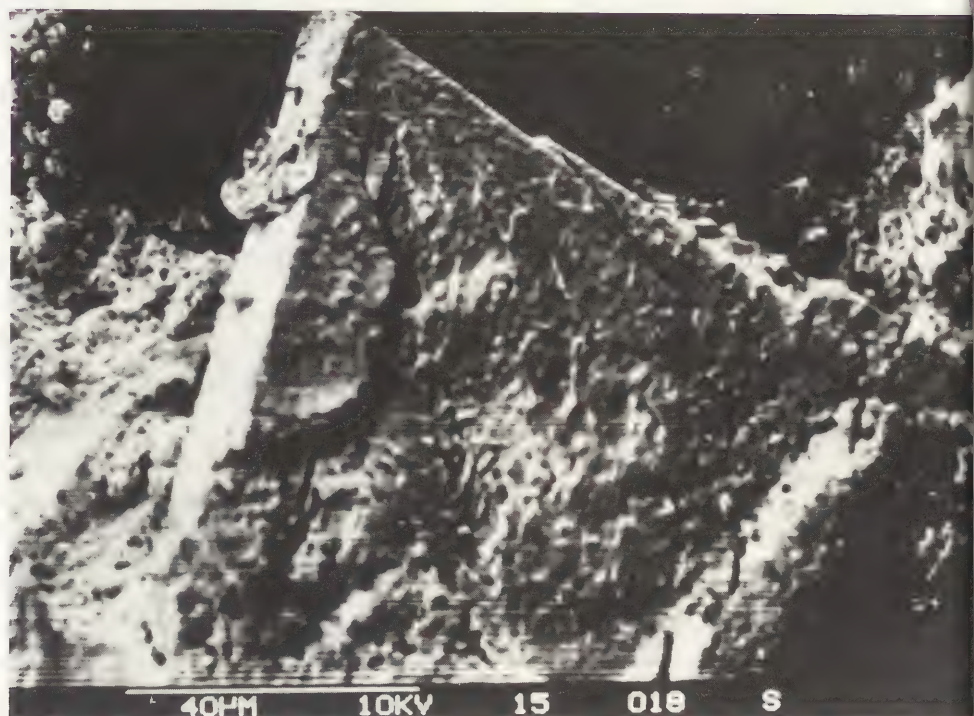


Figure 2. SEM photomicrograph of a fracture surface of the interior matrix of a plaster sample (TP2) showing a calcite crystal pseudomorph. The fissures visible on the pseudomorph originated during the lime-burning process.

Petrography was carried out on thin sections prepared according to NORMAL 12/83 recommendations (13). Figure 3 shows the interior matrix of a plaster sample (TP2).

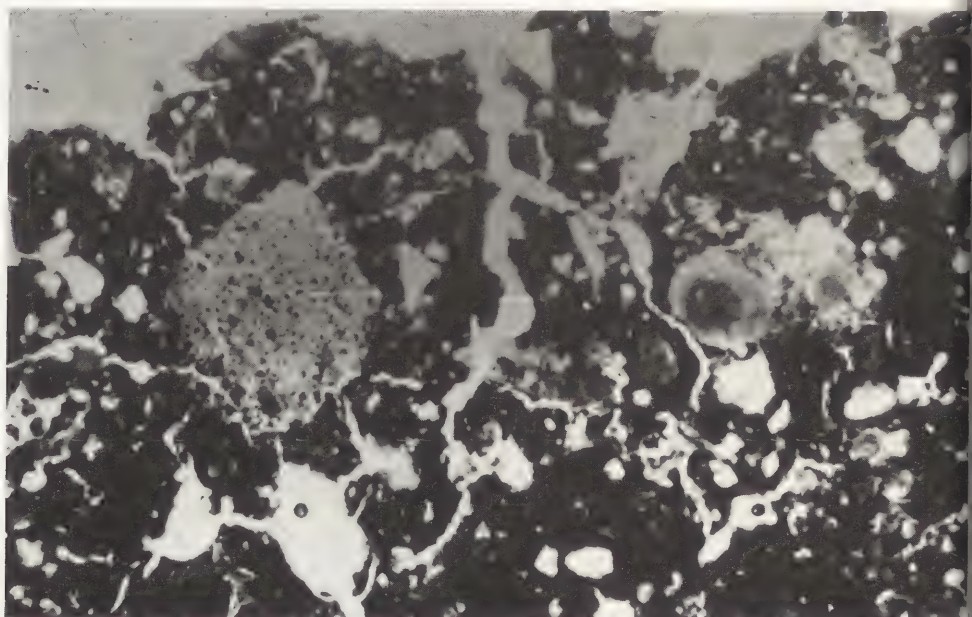


Figure 3. Thin section photomicrograph of the innermost layer of a plaster sample (TP2). Note the pores and microcracks perpendicular to the surface which account for the porosity of the plaster. Also to be observed is a large mass of presumably partially burnt lime. (// Nicol)

4. Infrared Spectroscopy

IR spectra were obtained from the powdered samples in KBr pellets. For comparison, standard samples of calcium carbonate were also run. The spectra were obtained between 4200 and 600 cm^{-1} .

The fine siliceous aggregates were separated by treating the samples with 1:4 HCl after removing the coarse aggregate. The KBr pellets prepared with the residue were scanned in the region of the Si-O-Si bending and stretching vibrations (1200-400 cm^{-1}).

5. Fiber Identification

The two mortar samples that showed the presence of fibers (TM3 and TM4) contained such small amounts that they could not be studied. The three plaster samples contained vegetable fibers in varying amounts. These were identified microscopically following an ASTM procedure (14).

Results and Discussion

1. Plasters

The samples of plaster examined had three distinct layers. The colour of the inner layer of the different samples varied from a whitish buff to a creamish white, while the external surface had a slightly greyish white colour, presumably due to the effect of weathering or the collection of dust and smoke.

One plaster sample (TP2) will be described in detail as representative for all of them. The thin section study showed that the external layer was a polishing layer of neat lime, about 1 mm thick, similar to the one shown in Figure 1. This layer did not contain any aggregate.

The middle layer had quartz and marble powder as aggregate in a binder matrix of microcrystalline calcite. It also showed some peculiar masses which appeared to be partially calcined limestone. This was confirmed by SEM studied which showed the presence of calcite crystal pseudomorphs with cracks induced during calcination (Figure 2). The poorly graded quartz grains ranged in grain size from 1/8 to 1/4 mm. They were subangular in shape with low sphericity. The aggregate/binder ratio was around 20% and the porosity, mainly due to cracks in the binder and in the masses of partially calcined limestone, was about 30%. The cracks formed perpendicularly to the surface of the plaster.

The innermost layer was composed of a mixture of lime and quartz with some mica, iron oxide and masses of partially calcined limestone. The quartz grains were well graded with grain sizes in the range of 1/16 to 1/8 mm. They were subangular in shape with medium sphericity. The aggregate/binder ratio was about 20% and the porosity, mostly due to rounded pores in the binder, was around 20% (Figure 3).

The examination of the vegetable fibers found showed them to be different in each sample. The main fibers found and identified (15) were sisal (*Agave Sisalana*) in TP1, jute (*Corchorus*) in TP2 and hemp (*Cannabis Sativa*) in TP3. All the fibers present are to be found in India and could have been used to strengthen the plaster. An interesting feature is that even after centuries, these fibers have not undergone alkali attack or any other form of decay.

XRD analysis showed that the plasters were basically constituted of calcite and quartz. The IR spectra showed the characteristic absorption bands for calcite (1425, 876 and 712 cm^{-1}) and a broad band at about 1080 cm^{-1} corresponding to quartz (16). The siliceous component was better analyzed on the acid insoluble residue and proved to be essentially quartz. The small quantities of mica as evidenced by XRD could not be confirmed by these spectra due to the low concentration of this mineral in the fine aggregate.

Results from the chemical analysis showed that there is quite a variation in the degree of carbonation of the plaster matrix. Variations in the silica content can be accounted for by variations in the proportion of calcareous/non-calcareous components in the aggregate and the fine sand used to prepare the plasters. The variations in the amount of the calculated hydraulic components, H, and its relatively high values appear to indicate that the lime used was partially hydraulic.

The amount of soluble salts present is not significant from a point of view of deterioration of the plaster. The amount of sulphates found, if originating from gypsum, as the prime salt produced by air pollution, would correspond to less than 1% by weight of this salt in the plaster, except for sample TP2, where it would correspond to 1.67%. It also has to be considered that gypsum could have been used as an admixture in the plaster. That this amount of gypsum is not causing any damage is confirmed by SEM and thin section examination where no evidence of the characteristic growth of gypsum crystals, as in deteriorating porous bodies, was found.

2. Mortars

The mortar samples were constituted of uniformly distributed binder and fine and coarse aggregates of various colours and textures. The colours ranged from a light buff to a reddish brown.

Thin section analysis showed them to be quite homogeneous with most of the mass made up of microcrystalline calcite with a few large crystals of calcite and quartz, and very little mica and feldspar. SEM showed that the binder of microcrystalline calcite was extremely fine grained and uniform, which may be due to the source of the lime, its slaking process and/or the fine grinding. The quartz grains were angular in shape with medium low sphericity and grain sizes around 0.1 mm. The porosity due to microcracks and pores in the binder was less than 20%. The pores were filled with recrystallized calcite and certain amorphous substances which may be hydraulic components. The coarse aggregate was found to be a mixture of different types of gravel and crushed stones. The gravels varied in colour from white to grey, brown and black. Their size was also quite large (up to 15 mm) and they varied in nature from calcareous to non-calcareous/siliceous.

XRD analysis showed them to be essentially lime mortars, dolomite, if present, being below the detection limit of the method. This composition was confirmed by IR analyses where the spectra showed the presence of calcite. The siliceous components, separated by acid treatment, showed only the presence of quartz, as mica and feldspar were in too low a concentration to be determined by this method.

Chemical analysis data showed that the degree of carbonation of the mortars is quite different in the different samples, and in general is less than that of the plasters, as could be expected. In correspondence, the amount of free lime found is larger. The magnesium content is fairly uniform as would be expected from a single lime source. The mortars appear to have been prepared with different mixtures of aggregate as indicated by the variation in the amounts of silica. The relatively high values of the calculated concentrations of the hydraulic components, H, indicate that the lime used contained a certain amount of them.

The main ions found in the aqueous extraction are chloride and calcium. The alkali ions present balance the amount of chlorides, and the calculated maximum amount of sodium chloride that could be present is found to be 1.36% by weight (TM2). The amount of gypsum calculated on the basis of the sulphate ions present corresponds to less than 0.80% by weight. These concentrations are not significant from a point of view of the deterioration of the material.

Conclusions

The detailed physico-chemical examination and instrumental analysis of the interior plaster and mortar samples of the Taj Mahal proved them to be lime based and that this lime was partially hydraulic.

The lime was well ground and the resulting carbonated matrix was extremely fine grained. The quartz grains were mostly well graded. Different types of aggregate, mainly sand gravel and pieces of stone, were used.

The porosity of the samples was low and was mainly due to microcracks. There were not many soluble salts present and this is in accordance with the fact that no sign of active deterioration was found in any of the samples.

Acknowledgements

This work was carried out during the period of study of the senior author in ICCROM, Rome. Thanks are given to the Director of this Institution for the fellowship provided, and to the Director of the Central Building Research Institute in India, for granting the leave.

The authors also want to acknowledge the staff of the Istituto Centrale della Patologia del Libro, for their cooperation in carrying out part of the experimental work in their laboratories.

Special thanks are due to Dr.G.Torraca for his helpful comments.

Bibliography

- (1) M.Asalam et al., "State of Conservation of Marble in Taj and Moti Masjid", Indo-US Subcommission Workshop on Conservation of Stone, Lucknow, January 1984
- (2) R.S.Tewari, "Conservation Problems of Taj Mahal", Indo-US Subcommission Workshop on Conservation of Stone, Lucknow, January 1984
- (3) Tecneco, Italy, "Studies for the Preservation of Monuments in Agra from Mathura Refinery Air Pollution" in III Report, 1976
- (4) Neeri, in Annual Reports of National Environmental Engineering Research Institute, Nagpur, India
- (5) M.Asalam, "Environmental Aspect of Taj", Seminar on Taj Mahal, Roorkee, India, 1984
- (6) K.S.Rao et al., "Air-Pollution Threat to Taj Mahal and its Environs due to Mathura Oil Refinery", Chemical Age of India 29 (8) 1978, pp. 663-674
- (7) K.S.Rao et al., "Short Term Pollution Threat of Mathura Refinery at the Taj and its Environs", Chemical Age of India 30 (10) 1979, pp. 903-907
- (8) ASI, in Annual Reports of Indian Archaeology, Research and Analysis
- (9) ASTM, Standard Method of Chemical Analysis of Limestone, Quick Lime and Hydrated Lime, ASTM C25, 1978
- (10) E.Cicconetti, in Analisi Technici, Elettrochimici, Sansoni, Florence 1979, pp. 443-445
- (11) A.E.Charola, M.Dupas, R.P.Sheryll, G.G.Freund, "Characterization of Ancient Mortars: Chemical and Instrumental Methods", Proceedings of the International Symposium "Scientific Methodologies Applied to Works of Art", Florence 1984, Arcadia, Milan 1986, pp. 28-33
- (12) M.Dupas, A.E.Charola, "A Simplified Chemical Analysis System for the Characterization of Mortars", Proceedings of the 2nd International Colloquium on Materials Science and Restoration, Esslingen 1986, pp. 309-312
- (13) NORMAL, "Aggregati Artificiali di clasti e Matrice legante non-argillosa. Schema di Descrizione", NORMAL 12/83, 1983
- (14) ASTM, Standard Method of Test for Fiber Analysis of Paper and Paper Board, ASTM D-1030, 1970
- (15) G.Poles, A.D.Giovanna, "Analisi Microscopica delle Fibre Naturali nella Carta", ATICELCA, Associazione Tecnica Italiana per la Cellulosa e la Carta, 1974, pp. 184-196
- (16) J.Bensted, S.P.Varma, "Infrared and Raman Spectroscopy in Cement Chemistry, Miscellaneous Applications", World Cement Technology 8 (1) 1977, pp. 16-20



SUMMARY

A cleanser has been developed for removal of microbiological stains from stone and other inorganic porous materials including frescoes. Comparative tests show it to be one of the most efficient, as well as least harmful to the original, of all methods and agents examined.

AN EFFECTIVE CLEANER FOR ORGANIC STAINS ON STONE

Zdravko Barov
Conservator
ETHOS, Inc
115 S. Topanga Cyn Blvd
Topanga, CA 90290 USA

Introduction

One of the most difficult problems encountered in the cleaning of stone artifacts is the removal of stains caused by microflora (mosses, algae, lichens, etc.) They can extensively discolor the surface and often penetrate through cracks, veins and large pores into the interior of the material. The dark stains are particularly noticeable on white marble where they cannot be partially camouflaged by the veining, color gradations or patterns found in multi-colored stones or frescoes. (Figures 1-6)

Traditional methods of treatment usually begin with application of a biocide in order to kill the growth (1-4). The next step is to attempt to remove the disfiguring stains. The cleaning techniques most often employed can generally be grouped into two main categories: those which lift the stains from the surface and those which do not actually remove the stains, but instead chemically convert them to invisible substances. Lifting (either by washing or dry mechanical removal) is best accomplished when the stain is concentrated on the surface and the substrate is smooth and sound. Bleaching is generally more useful when the growth has penetrated well below the surface or the surface of the artifact is already so deteriorated that it cannot support any further mechanical intervention. In many cases, it is best to employ both methods (5-9).

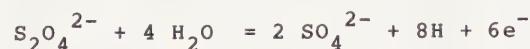
Unfortunately, however, many of the materials used today are only partially effective. Additionally, many substances and techniques (e.g. sandblasting, acids, airbrasive, etc.) which appear successful in removing the stain do so by damaging the original. This attribute, from our point of view, renders these methods equally unsatisfactory.

We have formulated a cleaning agent of the bleaching type ("Organic Stain Cleanser", hereinafter referred to as "OSC") which has proven effective when conventional methods have failed to bring acceptable results.

Discussion of the Composition and Properties of the Ingredients

This solution is based primarily on the bleaching effect of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), also known as sodium sulfoxylate and sodium dithionite. It functions as a reducing agent as follows:

- (1) reducing action of hydrosulfite



- (2) reduction of organic stain
stain + ne^- = colorless organic products

The bleaching action of the sodium hydrosulfite takes place more effectively in a basic solution where the acid product (H^+) is neutralized. Therefore, several buffers have been added to the main agent to absorb any excess acid and to stabilize the pH of the mixture to about 9.1. As will be seen in Table I, these buffers also eliminate the deleterious effect on the stone the sodium hydrosulfite has when used alone.

The buffers are: sodium carbonate (Na_2CO_3), anhydrous, monohydrate or decahydrate. Its aqueous solution has a pH greater than 7. Combined with sodium bicarbonate (as in this formulation), it forms an effective buffer with a pH of about 10; sodium bicarbonate (NaHCO_3), also known as sodium hydrogen carbonate. Mixed with sodium carbonate, the compound buffer can absorb any excess acid (to the limit of the buffer) accordingly: $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$; ammonium bicarbonate (NH_4HCO_3). In solution, this forms a relatively low capacity buffer with a pH greater than 7.

Another component of the system is a quaternary ammonium salt. Its primary function is to keep the solution free of any microbiological contamination. It also works as a cationic wetting agent.

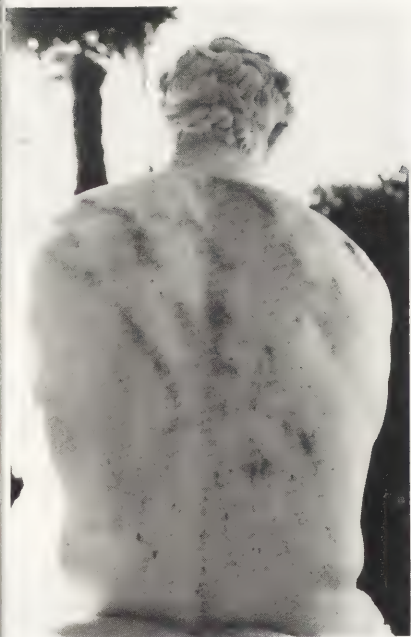


Figure 1. Carrara marble statue at Hearst San Simeon State Historical Monument. Stains have penetrated deep into the stone in crevices left by the dissolution of the more soluble inclusions.



Figure 2. Ornamental limestone urn from the Hearst San Simeon State Historical Monument. The lid is entirely covered with microfloral growth.



Figure 3. Detail of the north facade, Casa Grande, Hearst San Simeon State Historical Monument; microflora proliferate where the surface of the limestone is wet from rainwater.

The final ingredient of our formulation is a gel-forming agent. Although many different products can be used to give the cleanser a paste-like consistency (micronized silica, trisodium silicate, clays, etc.), we prefer the sodium salt of carboxymethyl cellulose ($\text{RnOCH}_2\text{COONa}$). Carboxymethyl cellulose is often used in detergent formulations as a soil-suspending and anti-deposition agent. Its main advantage in this situation is that it makes a transparent mixture, allowing one to continuously observe the bleaching process. We have found the high viscosity grade (1% aqueous solution at 25°C ; 1300-2200 centipoises) to be the most suitable for this application.

The development of a successful cleanser was guided by three major objectives: it had to be safe for the stone, safe for the user, and effective in removing resistant stains. Formulations were tried in varying concentrations and proportions. Individual ingredients were added and then discarded when they failed to satisfy one or more of the objectives. Some important factors which we considered were the effect of the cleanser on the surfaces of marbles and frescoes, its effect on pigments (particularly earth pigments) and the amount of penetration of the gel and rinse-water into the treated object. Table I shows the results of tests made during this formulation process in order to determine the action on the stone of several of the active ingredients when used singly or in combination. Polished pieces of white marble were immersed in the various combinations for a period of 24 hours and were then examined under the microscope. The relative effects are detailed below:

TABLE I

	+++ pronounced erosion of the surface + slight erosion	++ some erosion - no observable erosion
sodium hydrosulfite (10% aqueous solution)		+
sodium tripolyphosphate (10% aqueous solution)		+
EDTA disodium salt (10% aqueous solution)		+
distilled water		+
OSC		-
OSC with sodium tripolyphosphate		+
OSC with EDTA		+

It is interesting to note that buffering all three active ingredients significantly reduces their impact on the stone without lessening their effectiveness against the stain. This is especially noticeable with the sodium hydrosulfite. The addition of EDTA or sodium tripolyphosphate to OSC did not (contrary to our expectations) substantially improve the effectiveness of the cleanser on organic stains - and each made the compound more harmful to the marble than the OSC alone. Distilled water was included in the testing because, although its solvent action on calcium carbonate-containing stones has been well-documented, its use is still widespread in conservation practice.

Comparative Tests

The effectiveness of the final formulation of the OSC was compared to several commonly used cleaning and bleaching substances on strongly contaminated white Carrara marble samples as well as a white Carrara marble relief in situ. Results of the tests are summarized in Table II.

TABLE II

	+++ almost complete removal + some effect	++ partial removal -- no effect
OSC		+
AB 57		+
Hydrogen peroxide, 40%		+
Chloramine-T		+
Chlorine dioxide		+
Calcium hypochlorite		+
Distilled water		--
Magnesium silicate pack		--

AB 57 is a general cleaning agent (9) very efficient against surface stains, particularly those associated with salt crystallization. However, because its main active ingredient, EDTA, reacts with calcium carbonate, it (as was shown in Table I) is often harmful to those materials which contain CaCO_3 . Additionally, it is ineffective against deep stains which occur in the matrix of the material.



Figure 4. Carrara marble relief with northwest exposure, Hearst San Simeon State Historical Monument. (See details below)



Figures 5 & 6. Details of Figure 4, showing the particularly intense staining that occurs at the base of the relief where large quantities of water run over the stone.



Hydrogen peroxide is an oxidizing bleach which is often very effective in removing deep stains of microbiological origin. Its primary drawback is that it will oxidize any iron particles already in the stone, causing non-removable rust stains.

Chloramine-T is a bleaching agent which has to be applied repeatedly to achieve results. Its rapid decomposition makes it safe for use on stone because it does not leave harmful residues, but it is relatively inefficient in removing resistant stains. Test applications were with fresh 2% aqueous solutions.

Chlorine dioxide is very dangerous for the user (and potentially for others in the area). In general, its employment is to be avoided. It is not as effective a cleanser as other substances and, because elaborate safety precautions must be taken, is difficult to use.

Calcium hypochlorite proved very efficacious against both surface and deep stains. For the tests, a 0.8% aqueous solution of calcium hypochlorite (available chlorine 65%) was used. It was neutralized after application with a 2% solution of sodium thiosulfate. The main disadvantage of the use of this method is that it leaves residues of sodium chlorite and calcium sulfate which remain in the stone after treatment.

Directions for Preparation and Use of OSC

The cleanser is compounded in the following proportions:

- 1,000 cm³ cold deionized water*
- 50 grams sodium hydrosulfite
- 50 grams sodium carbonate
- 50 grams sodium bicarbonate
- 30 grams ammonium bicarbonate
- 1 gram quaternary ammonium salt
- 38 grams carboxymethyl cellulose sodium
- * water temperature should not exceed 30°C

To prepare it, the sodium hydrosulfite, sodium carbonate, sodium bicarbonate, and the quaternary ammonium salt should be slowly added to the water while stirring continuously. After these are completely dissolved, the carboxymethyl cellulose should be added very gradually while constantly stirring the mixture to avoid lumping. Some lumps will form even with this method of preparation. It is best to allow the mixture to rest overnight before use as the majority of lumps will dissolve in this time. If stored in a well-closed container, this cleanser has a shelf life of at least one year.

The recommended application time is 15 to 20 minutes. After this time, the cleanser should be carefully removed with a damp cotton swab. The surface should then be rinsed well with water-soaked cotton swabs. This application can be repeated several times if necessary until satisfactory results are obtained. In our practice, the stains start to fade rapidly 10-20 seconds after application. OSC works only to remove the stain. A biocide should be applied both prior to and immediately after application to ensure the elimination of any microorganisms.

The relative amounts of the components of the cleanser can be varied considerably. Changing the amounts of the carboxymethyl cellulose changes the viscosity. In general, we have found the amount given above to provide the most easily handled gel. Reducing the sodium hydrosulfite concentration to 1% produces a less effective cleanser, since longer times and repeated applications become necessary to produce the same affect. The proportions of the buffering agents can be varied without noticeable effects, but at low concentrations, the buffering capacity may be exceeded. The amount of the quaternary ammonium salt should not be changed drastically because this minimum amount is needed to maintain the fungicidal properties and a too high a concentration might pose health hazards.

Considerations for User Safety

All of the components of OSC have very low toxicity levels. LD₅₀ values range between 4,000 and 27,000 mg/kg. However, because some of the dry ingredients can be skin and eye irritants, it is recommended that goggles, gloves and dust masks be used during preparation. For application, only gloves are required. Cold water (below 30°C) should be used in preparation of the mixture due to the incompatibility of sodium hydrosulfite with hot water (10).



Figure 7. Detail of the top of the relief shown in Figure 4. Four areas were test cleaned with (from top to bottom): calcium hypochlorite, AB 57, hydrogen peroxide, and Chloramine-T.



Figure 8. Detail of Figure 4 after test cleaning with sodium sulfite-based cleanser (OSC) on the left, and chlorine dioxide to the right.

Conclusions

In comparison to other typical cleaning formulations, this cleanser seems to be more efficient against resistant organic stains and less harmful to original materials, particularly those which are weathered and/or reactive. It does not require any scrubbing or rigorous brushing to be effective, unlike wet or dry mechanical removal methods which often remove particles of the original along with the particles of stain matter. Additionally, this preparation represents little health hazard for the user.

OSC is effective primarily because of the reducing property of sodium hydrosulfite. The high pH required for this reaction to be most efficient is assured by the addition of sodium carbonate and bicarbonate and, to some extent, by the ammonia/ammonium ion buffers. Although the compound contains no detergent in the strictest sense, carboxymethyl cellulose sodium salt is often added to detergent preparations to aid in suspension of the soil and the action of it and the sodium carbonate is similar to that of detergent. The carboxymethyl cellulose also serves to minimize the penetration of the oxidized organic material into the treated object because of its anti-deposition character.

The cleanser is equally effective on stains on frescoes and mortars, but should be used only if no organic components are present in the substrate.

Acknowledgment

The author wishes to acknowledge the generous assistance of Dr William Wilk, Professor of Chemistry, California State University, Dominguez Hills.

References

1. Grand, C. and Bravery, A.F., "A New Method for Assessing the Resistance of Stone to Algal Disfigurement and the Efficacy of Chemical Inhibitors", Vth International Congress on Deterioration and Conservation of Stone Vol 2, Presses Polytechniques Romandes, Lausanne (1985) 663-669.
2. Richardson, B., "Control of Moss, Lichen and Algae on Stone", The Conservation of Stone I, Proc. Int. Symp., Centro per la Conservazione delle Sculture all'Aperto, Bologna (1976) 255-231.
3. Sharma, B.R.N., et al., "Biological Growth Removal and Comparative Effectiveness of Fungicides from Central India Temples for a Decade In Situ". Vth International Congress on Deterioration and Conservation of Stone Vol 2, Presses Polytechniques Romandes, Lausanne (1985) 675-683.
4. Wainwright, I., "Lichen Removal From An Engraved Memorial to Walt Whitman", APT Bulletin, Vol XVIII No. 4, (1986) 46-51.
5. Amoroso, G. and Fassina, V., Stone Decay and Conservation, Elsevier, Amsterdam (1983) 270-296.
6. Gibson, B.M., "The Use of the Airbrasive Processes for Cleaning Ethnological Materials", Studies In Conservation 14, (1969) 155-164.
7. Hempel, K., "The Biological Pack", Alteration et Protection des Monuments en Pierre, UNESCO-RILEM, Paris (1978).
8. Lehman, J., "Quelques Nouvelles Recherches sur le Nettoyage et la Preservation des Sculptures en Pierre Exposees a l'Exterieur en Pologne", The Conservation of Stone I, Proc. Int. Symp., Centro per la Conservazione delle Sculture all'Aperto, Bologna (1976) 477-483.
9. Mora, P. and Mora, L., "Metodo per la Rimozione di Incrostazioni su Pietre Calcaree e su Dipinti Murali", Problemi di Conservazione, Editrice Compositori, Bologna (1971) 339-344.
10. Sax, N. I., Dangerous Properties of Industrial Materials 6th edition, Van Nostrand Reinhold Co., New York (1984).

SUMMARY

In order to assess the influence of soluble salts (especially NaCl and MgSO_4) on the efficiency of a conservative treatment of a porous stone (in this case Vicenza stone) some samples of quarry stone have been soaked with saturated solutions of NaCl and MgSO_4 by capillarity rising. Surface and deep treatments have been afterwards carried out on these samples by methylphenylpolisiloxane. The successive salt release, monitored by using conductometric method, has been used to test the efficiency of the treatment. Water absorption tests have also been performed on a series of analogous saturated samples.

INFLUENCE OF SALTS ON THE EFFICIENCY OF A CONSERVATIVE SILICONIC TREATMENT ON STONES

G. Biscontin, A. Masin, R. Angeletti

Department of Chemistry, University of Padua (Italy)

G. Driussi

Department of Chemistry, University of Venice (Italy)

Introduction

The use of siliconic compounds as "consolidant" and/or "protective" products in the conservation of stone is very frequent (1). Generally the tests to verify the efficiency of these products include a set of solicitations and artificial ageings carried out on samples of quarry stone (2, 3, 4).

In fact measurements on naturally degraded samples are not reliable owing to their heterogeneity. It is for this reason that, within a more complex study on the efficiency of silicone in stone conservation, we have tried to evaluate the possible effect of salts naturally present in the stone on the efficiency of the product (5, 6, 7, 8).

To this end two salts of peculiar interest have been examined: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and NaCl (9), the former owing to its crystallization with volume variation (9), the second owing to its importance as an element of degradation, also as a consequence of our group's interest for the problematics concerning the city of Venice (10, 11, 12).

The choice of the above mentioned salts for the reproduction of degradation phenomena, instead of the seemingly most suitable CaSO_4 (13), is due to its low solubility and the consequent non significant amount of salt present in impregnated samples.

Experimental section

In order to simulate the effect of "salification" connected with the progressive deterioration of stony materials, two series of samples (5x4x1.5 cm) have been saturated with solutions of NaCl (25% in weight) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (40% in weight) respectively, using NORMAL procedures (14, 15).

After the impregnation the samples have been washed out superficially with deionized water, dried with absorbent paper and finally left in an airy room to dry at the temperature of 25°C for ten days.

After this period they have been put into a dryer until their weight became constant for a mg. carrying out two weighings at the distance of 24 hours one from another.

It has been possible to obtain an average value of impregnation, expressed in weight %, of about 4.7-5.0% for MgSO_4 and 2.7-3.0% for NaCl, that is to say values approximately corresponding to an initial stage of a deterioration process (see tables n.1 and 2)(5). These samples, as well as other analogous ones prepared in the same way but not saturated with salt solutions, have been treated with methylphenylpolisiloxane at three different concentrations (5%, 10% and 20% in 1,1,1-trichloroethane) and with two different application techniques, namely by brushing and by capillarity.

Sample	Conc.	W (gr)	% S/W	% R/WS
1	5%	65.708	5.272	0.747
2	10%	62.836	4.970	1.057
3	20%	71.268	4.804	2.469
4	5%	55.857	2.662	0.872
5	10%	67.584	2.785	0.973
6	20%	64.388	3.091	3.641

Table 1 - Samples protected by capillarity (1, 2, 3 saturated with MgSO_4 solution; 4, 5, 6 saturated with NaCl solution). Each value reported in table is averaged over three different samples.

S: amount of salt; R: amount of protective.

Sample	Conc.	W (gr)	% S/W	% R/WS
7	5%	65.668	5.024	0.659
8	10%	62.834	5.004	0.650
9	20%	66.611	4.783	0.868
10	5%	62.418	2.945	0.164
11	10%	62.631	2.931	0.238
12	20%	131.250	3.177	0.163

Table 2 - Samples protected by brushing (7, 8, 9 saturated with $MgSO_4$ solution; 10, 11, 12 saturated with $NaCl$ solution). Each value reported in table is averaged over three different samples.

S: amount of salt; R: amount of protective.

in this way we obtained two series of samples, a first group of samples artificially aged and successively treated with methyl-phenylpolisiloxane; a second group of samples treated with the protective agent but not saturated with salts, taken as a reference. The tests performed on the samples, had the aim of determining the protective efficiency, both from the point of view of the water-repellency and from the point of view of its capacity to prevent salts release by the stone.

In the first place we considered water absorption in the course of time in totally immersed samples.

In order to control the possible release of salt by the stone during immersion, we have carried out conductivity measurements which, although not selective, are, nevertheless, sensible enough for this kind of determinations.

We expected conductivity curves, corresponding to the release of salts, to be very flat initially and assumed growing values only after a long period of time; on the contrary we found an immediate solubilization of the inner salt.

In fact as a matter of fact, conductivity values reach in a very short time the 50-60% of the final conductivity.

Confronting the final conductivity with the calibration curves, determined for the salts we had used, we find that the salt contained inside the samples releases itself in a quantitative way almost systematically.

These results are confirmed by the chemical analysis of Mg and Na, present in the solution which the samples had been bathed in. If we consider the efficiency of a protective product as directly related to its capacity to prevent the water access into the samples, in order to have homogeneous comparisons we can define

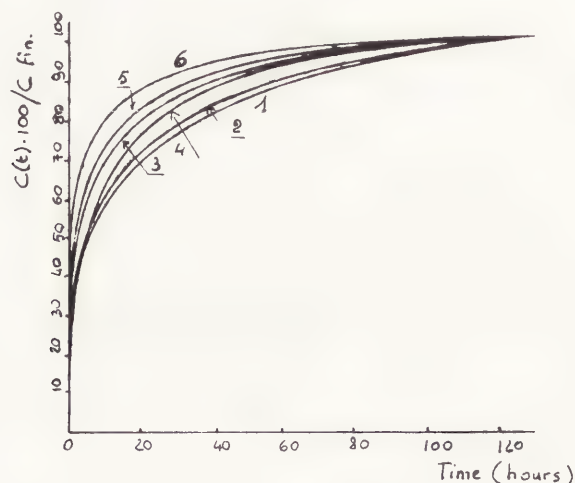


Fig.1 - Conductivity curves regarding capillarity treatment (1, 2, 3 are samples saturated with $MgSO_4$ and protected with resin at 5%, 10% and 20% in weight respectively, while 4, 5, 6 are saturated with $NaCl$ and protected with resin at the same concentrations of the previous ones)

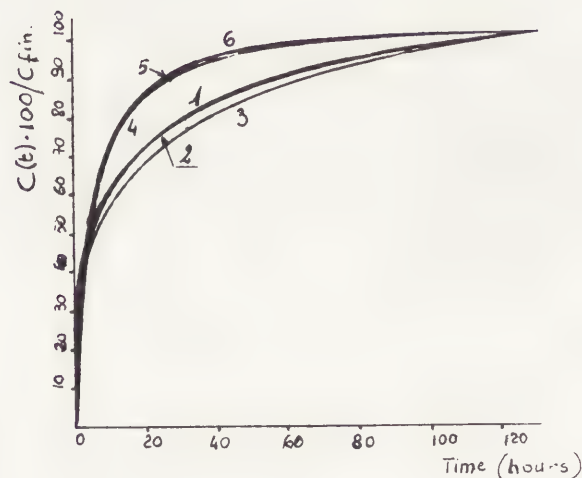


Fig. 2 - Conductibility curves regarding brushing treatment (1, 2, 3 are samples saturated with MgSO_4 and protected with resin at 5%, 10% and 20% in weight respectively, while 4, 5, 6 are saturated with NaCl and protected with resin at the same concentrations of the previous ones)

the efficiency, or better the loss of efficiency, as the ratio between the measurements of conductivity after 24 hours and at the final time.

In fig. (1) and (2) it is possible to notice one main difference - even if not especially pointed out - between the curves referring to the samples saturated respectively with NaCl or with MgSO_4 . In all the observed cases, the former lose the salt more quickly than the latter - especially in short times -.

It has also to be noticed that with either salts efficiency - as defined above - decreases in a way which is not significantly linked with the concentration used.

Moreover, the graphics show no apparent difference even as regards the modes of application of the protective.

For a further confirmation of the previous results we also carried out water absorption tests by total immersion, on a series of samples, some of which prepared in the same way as the ones used for the conductivity measurements, and some others treated with the protective - using an average concentration rate and applied in both ways - but not saturated with salt.

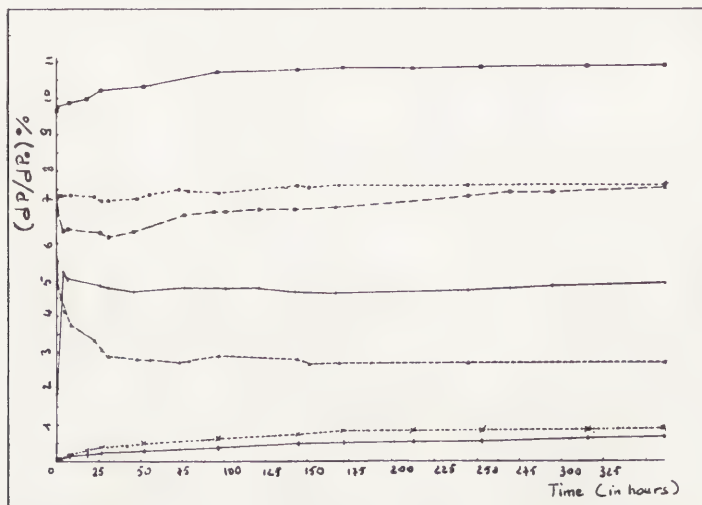


Fig. 3 - Absorption of water curves (1: untreated sample; 2: treated with the resin by capillarity; 3: treated with the resin by brushing; 4: saturated with MgSO_4 and protected by capillarity method; 5: saturated with MgSO_4 and protected by brushing method; 6: saturated with NaCl and protected by capillarity method; 7: saturated with NaCl and protected by brushing method)

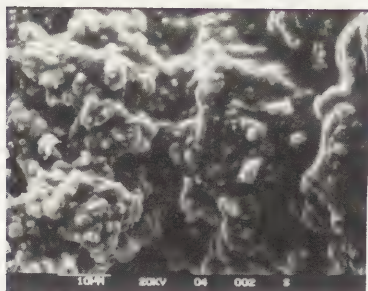


Fig. 4 - Vicenza stone protected with methylphenylpolisiloxane by capillarity (1500 x)

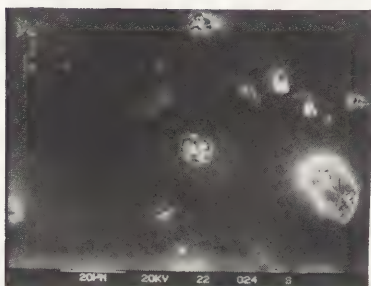


Fig. 5 - Vicenza stone treated with $MgSO_4$ solution and protected with methylphenylpolisiloxane by capillarity (1000 x)

Per cent values of weight variations (fig. 3) prove the water repellent effect of the siliconic compound. However from what is shown in the figure we can detect the occurrence of the twofold process already pointed out by conductivity measurements, namely the intake of water as well as the complete discharge of salt. The sum of these two concomitant effects gives the curves in figure and it is possible to notice that for NaCl there is an initial decrease in weight %, due to the solubilization of the salt that is not counterbalanced by the water absorbed.

At the end of our tests we also carried out a SEM examination on some samples of stone artificially "salted" and then treated with the protective, as well as on some others simply treated with the resin (all the observed specimens had been protected by capillarity method).

From the reported photographs it is possible to point out that in the quarry samples there is a uniform layer all over the surface (fig. 4) but, on the contrary, protective film doesn't succeed in uniform and complete adhesion when a protective treatment is carried out on an artificial aged samples (fig. 5).

The described anomalous behaviour of the samples toward water action, can be so explained by these observations that relate the superficial presence of soluble salt crystals to a lacking protective action by methylphenylpolisiloxane.

Conclusions

First of all it is possible to say that the presence of soluble salts inner a stone has opposite effect toward the efficiency of a conservative treatment.

In second place we can say that NaCl, with its mobility, is more dangerous toward the kind of treatment examined than $MgSO_4$, in spite of the volume variations related to its hydration degree, on the contrary to what can be supposed in a first approach.

Moreover we can say that the application methods and the concentrations are not critical parameters and have no substantial influence on the efficiency of the treatment and that the natural development of this study will be an investigation of other different kinds of products and the attempt to analyse the adhesion problematic that came out from our tests.

References

1. Hanna S.B., The use of organosilanes for the treatment of limestone in an advanced state of deterioration. Preprints of the International IIC Congress "Adhesives and consolidants", Paris 1984 pp. 171-176.
2. De Witte E., Charola A.E., Sherry R.P., Preliminary tests on commercial stone consolidant. "Vth International Congress on deterioration and conservation of stone", Losanna 25-27/9/85 pp. 709-718.
3. Sramek J., Perina V., Sensitive evaluation of the conservation efficiency of materials used for the treatment of stone. "Vth International Congress on deterioration and conservation of stone", Losanna 25-27/9/85 pp. 553-560.
4. De Witte E., Huget P., Van Der Broek P., A comparative study of three consolidation methods. "Studies in Conservation" Vol. 22, 1977 pp. 190-196.
5. Driussi G., Valle A., Biscontin G., Porosity and soluble salts as decay parameters of stone materials. "Vth International Congress on deterioration and conservation of stone", Losanna 25-27/9/85 pp. 185-189.
6. Binda L., Baronio G., Charola A.E., Deterioration of porous materials due to salt crystallization under different thermohygrometric conditions I. Brick. "Vth International Congress on deterioration and conservation of stone", Losanna 25-27/9/85 pp. 279-288.
7. Krantz M., L'evaluation de l'etat de conservation de la pierre

et de l'efficacite' des traitements. The Conservation of stone I, Proceedings of the International Symposium", Bologna 19-21/6/75 pp. 443- 553.

8. Arnold A., Soluble salts and stone weathering. "The Conservation of stone I, Proceedings of the International Symposium", Bologna 19-21/6/75 pp. 133-135.

9. Kirk-Othmer, Encyclopedia of Chemical Technology, ed. J. Wiley and Sons, 3rd ed. (New York, 1980)"sodium compounds and magnesium compounds".

10. Badan B., Marchesini L., Natile G., Sulla presenza di sali solubili nelle murature di un edificio veneziano. "IIIrd International Congress on the deterioration and preservation of stones", Venezia 24-27/10/79 pp. 165-173.

11. Chatterij S., Christensen P., Overgaard G., Mechanisms of breakdown of natural stones caused by sodium salts. "IIIrd International Congress on the deterioration and preservation of stones", Venezia 24-27/10/79 pp. 131-134.

12. De Vecchi Gp., Lazzarini L., Menegazzo Vitturi L., Deterioration due to salt efflorescence on interior marble facings of the Church of S. Maria dei Miracoli, Venice. "The Conservation of stone II, preprints of the contributions to the International Symposium", Bologna 27-30 /10/81 pp. 417-439.

13. Puehringer J., Berntsson L., Hedberg B., Hydrate salts and degradation of materials. "Vth International Congress on deterioration and conservation of stone", Losanna 25-27/10/81.

14. Documento NORMAL 7/81: Assorbimento d'acqua per immersione totale - capacita' di imbibizione.

15. Documento NORMAL 13/83 Dosaggio dei sali solubili.



SUMMARY

In the course of excavation of the Crypt of Balbus in Rome, conservation and maintenance treatments were carried out on a structure in tuff partly covered with plaster on one side and shouldered by an embankment on the other side.

The problem of crystallization of soluble salts was addressed by applying a lime-wash on the tuff blocks. The lime-wash served not only as a "sacrificial surface" but also as a means of rendering the history of the wall more legible to visitors.

A STRUCTURE OF TUFF BLOCKS: TREATMENT FOR DISPLAY

Andreina Costanzi Cobau
Centro di Conservazione Archeologica (C.C.A.)
Via Zanardelli 16, 00186 Rome, Italy

Behind the stage of the Theatre of Balbus, located in the urban centre of Rome, was an extensive area composed of a rectangular courtyard surrounded by cryptoporticoes: the Crypt of Balbus.

The Crypt of Balbus was the object of a careful archaeological investigation, which brought to light facts and evidence necessary for the understanding of the history of the site in its successive phases of use, abandonment, and re-use (1).

In the context of the excavation, periodic maintenance and conservation treatments were carried out on a structure in tuff, partially covered with plaster. This site exhibits the various problems encountered in the excavation phases and the conservation solutions chosen, both of a temporary and final nature.

The cryptoportico is closed on the west side by an exedra, which, because of the imposing presence of the surrounding walls (two-thirds of which remain), has lent itself to various re-uses, which have altered its appearance and even part of its original materials.

Description

The area is defined by a rectilinear wall of brick and a semicircular wall of blocks (*opera quadrata*) of travertine and tuff (Plan). In the course of the excavation of the tuff blocks, traces of various layers of plaster facing were found, close to some cavities that held marble wedges, which might have served as clamps for a heavier facing. It is difficult to tell now which was the original facing.

A modern superstructure of cement, which repeats the semicircular form of the wall underneath, was all that could be seen at the beginning of the excavation, when the ground level was 8 meters higher than that of the Roman era.

Behind the block wall is a flat embankment, used as a parking lot and loading zone, which reaches almost to the height of the wall itself. The brick wall separates the exedra area, site of one of the excavation trenches, from another trench area in the courtyard.

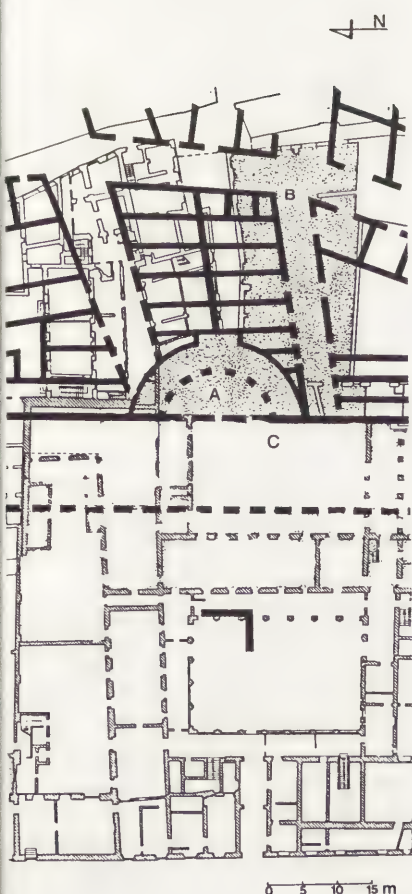
Prevention

It was evident that the exedra, completely surrounded by walls, had no drainage facilities for rainwater, once the excavation began. Therefore a temporary transparent roofing was installed, limited to the area described, in order to protect it from atmospheric precipitation and to prevent water from collecting in the exedra. The roofing was designed to carry off the water through a drainpipe with a gutter, rather than along the side of the sloping roof, and was raised above the height of the brick wall in order to permit internal air circulation, so that the thermohygrometric values for the covered environment were as close as possible to those of the adjacent environment (2). Some differences in thermohygrometric values were observed, however, between the different areas, in all seasons, up to as much as 10°C.

The space between the roof and the top of the brick wall was also left open for the convenience of visitors, to permit observation, from a scaffold, of the exedra from above (Fig. 1).

State of conservation

It is easy to imagine how the conservation problem of the exedra was concentrated along its perimeter, in particular along the tuff inner wall of the semicircular structural wall. The rectilinear wall, in fact, did not present any conservation problems, given that both sides were excavated gradually, permitting the whole structure to dry. It was only necessary, during the excavation of the courtyard, to avoid the creation of hollows in the ground along the brick wall, areas which might have caused pockets of humidity, resulting in disequilibrium with respect to the inner wall of the exedra. On the contrary, the water infiltrations coming from the embankment behind the block wall, which before the excavation formed a stable situation



Plan: The site of the Crypt of Balbus.

- A - Exedra area
- B - Embankment
- C - Garden area

(Source: D. Manacorda, *Il Giardino del Conservatorio di S. Caterina della Rosa*, Firenze, 1984.)



Fig. 1: Exedra area, view of the southwest corner with the passage over the rectilinear wall.

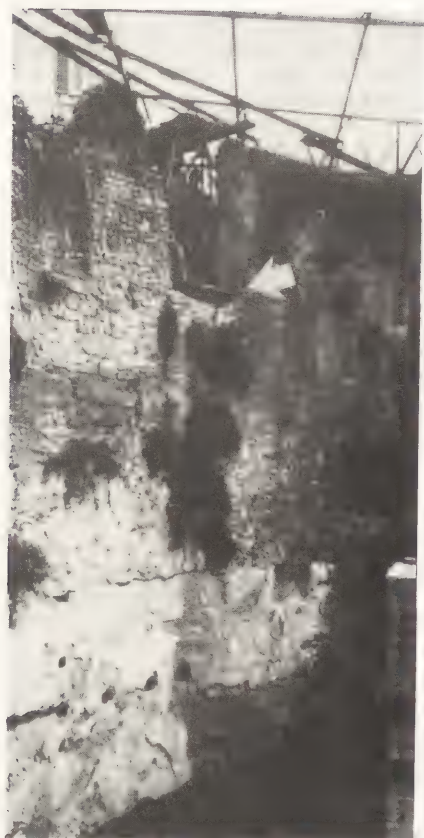


Fig. 2: View of the wall of tuff blocks. The arrow indicates the level of the embankment behind the wall.

between the tuff, the plaster that partially covers it, the soluble salts in the water and the ground, now create a continuous cycle of evaporation-condensation on the surface level resulting in soluble salt crystallization phenomena.

Thus the tuff inner wall has become a delicate diaphragm between two environments characterized by very different climatic situations: one, that of the rear embankment, which we can define as stable in the quantity of humidity brought to the wall itself; the other, that of the excavation area in the exedra subject to climatic variations by day and night, seasonal variations, and those linked to excavation activities (Fig. 2). The only filter for this disequilibrium is the block wall with the cement superstructure.

The inner wall is very heterogeneous: the tuff blocks with various remains of different facings present various stages of conservation. We note how the disintegration and the detachment of the plaster are concentrated along the outer edges of the fragments, while the greatest spalling of the tuff occurs near the most compact plaster. It is evident that the front line of evaporation of humidity coming from behind varies according to plaster or tuff: the different porosity of the materials has determined micro-movements of water near the points of contact between the two materials, forming a concentration of humidity along the outer edges of plaster fragments as they are preserved *in situ* (3). The tuff, where it was not faced with plaster, fell in scales as thick as 5 cm.

Treatment

In the course of the excavation, steps were taken to treat the roughness of the surface of the tuff, by plastering the cracks and hollows and readhering the scales with hydraulic mortar (4) (Fig. 3). Reducing the surface roughness partly eliminated the infestation of insects and plant growths that had found a rich substratum of humidity in the tuff.

The continual cycle of evaporation-condensation remained however, a significant cause of deterioration for the inner wall of tuff and for the plaster. Unable to do much about the humidity coming from behind, we had to accept the infiltration as a "given" and find a solution between plaster and tuff.

During the excavation phase, no definitive steps were taken until the wall in question was completely exposed. The process of excavating by strata (5), in fact, forced us to consider, in addition to the vertical levels of tuff and plaster facing, also the horizontal ground planes and resultant bands of evaporation through capillary rise. These two "characteristic horizontals" should be seen as movable, according to the progress of the archaeological excavation: regular progress during the normal work season, interrupted during the winter recess. We tried, therefore, to avoid any further deterioration that might be caused by the level of soil immediately supporting the tuff wall; in particular, when the remains of the plaster facing were brought to light, they were protected with damp compresses of cellulose pulp, in order to displace the band of evaporation due to capillary rise onto the tuff (6).

In contrast, the front line of evaporation of the humidity coming from behind was and is always uniform, above a heterogeneous surface of materials of different porosity. Once the problems of the surface roughness and the rising damp were overcome, we were faced with a surface singularly characterized by two materials of different porosity: the tuff, which presents the greatest extent of exposed surface area and is a material with very small pores that absorb humidity very slowly; and the plaster, with pores of a larger diameter permitting a more rapid evaporation (7). The tuff blocks, permeated with water practically all year, exhibit a dry surface layer only in the summer months, but at the same time they also crystallize the soluble salts contained in the water, so that the surface becomes covered with a layer of efflorescence, and the tuff next to the plaster layer falls in scales.

The solution chosen was to bring the whole tuff wall to a surface porosity similar to that of the plaster, creating a "sacrificial surface" on which the soluble salts carried by the infiltration from behind can crystallize without damaging the stone. A compromise between plaster and tuff was sought: a coat of porous, water-permeable material, a lime-wash (8) (100 cc slaked lime, 500 cc water, 3 cc pigment, natural earth umber), applied onto the surface of the tuff not already covered with plaster (Fig. 4).



Fig. 3: Detail of a tuff scale consolidated with hydraulic mortar.

This wash, with a basic pH that also served to inhibit micro-organisms, made the behaviour of the entire inner wall more homogeneous with respect to the evaporation-condensation cycle, which now took place in a uniform manner instead of being concentrated along the perimeter of the ancient facing.

This kind of solution requires frequent maintenance, given the low mechanical resistance of the wash; thus we foresee a 3-4 year cycle of reapplication and a seasonal inspection to avoid the growth of micro-organisms, especially algae.

Final considerations

At this point, we can say that we have obtained the necessary results, but it must be considered that while on the one hand the damage from salt crystallization on the surface is prevented, on the other hand the non-transparent protective coating changes the appearance of the wall structure. Before applying it, therefore, we studied the character of the tuff blocks as architectural elements. Such blocks are found above a series of rows of travertine and must have originally been faced either with marble slabs or with plaster frescoed to imitate marble, as the remaining traces demonstrate.

The wash takes the place of a facing which surely covered the entire inner wall in the past, of which only a few fragments remain today, scarcely legible but useful as a model for the treatment. The colour of the wash, in fact, was chosen to resemble the plaster fragments, and the whole inner wall now presents a more homogeneous appearance from a chromatic point of view (Fig. 5)

We might conclude by noting that the failure to treat the back of the structural wall, or to do something about the origin of the deterioration, might make our solution appear futile, with little probability of success. The writer is convinced that a true conservation treatment is characterized by attacking the problem of deterioration at its source, but this is not always possible, as in this case, given the impossibility of excavation behind the wall.

This treatment should therefore be seen as the consolidation of a tuff wall, not a long-term solution, but one that will require regular inspection in the future on the part of the conservator.



Fig. 4: Application of the lime-wash on a block of tuff.



Fig. 5: General view of the inner wall 10 months after the lime-wash treatment.

NOTES

1. D. Manacorda, Archeologia urbana a Roma: Il progetto della Crypta Balbi (Firenze: Edizioni all'Insegna del Giglio, 1982).

This corresponds to the city block formed by Via Caetani, Via delle Botteghe Oscure, Via dei Polacchi, and Via dei Delfini. The work began in November 1981, and is directed by M.L. Conforto of the Archaeological Superintendency of Rome and by Prof. D. Manacorda of the University of Siena. To date, a variable number of archaeologists -- researchers, graduates, students -- from various Italian universities have participated in the excavation, up to a maximum of 70 per campaign. There have been six campaigns interspersed with laboratory research activities. The results of the work are published contemporaneously with the excavation: three volumes are already available, and three others are in preparation. The intervention was carried out by M. Anastasi, A. Costanzi Cobau, L. Demitry, R. Nardi, C. Tavazzi, M. Van Molle, of the Centro di Conservazione Archeologica (C.C.A.), Rome.

2. R. Nardi, "Conservation on the Excavation: the Crypt of Balbus in Rome", Preventive Measures during Excavation and Site Protection, Conference, Ghent, 6-8 November 1985 (Rome: ICCROM, 1986), p. 91-110.

3. G. Torracca, Porous Building Materials: Materials Science for Architectural Conservation (Rome: ICCROM, 1982).

4. D. Ferragni, M. Forti, J. Malliet, J. M. Teutonico, G. Torracca, "In situ consolidation of wall and floor mosaics by means of injection grouting techniques", Mosaics no 3: Conservation in situ [Conference], Aquileia, 1983 (Rome: ICCROM, 1985), p. 83-101.

5. P. Barker, Techniche dello scavo archeologico (Milano: Longanesi, 1981).

6. P. Mora, "Conservation of excavated intonaco, stucco and mosaics", Conservation on Archaeological Excavations (Rome: ICCROM, 1984), p. 97-107.

7. G. Accardo, S. Massa, P. Rossi Doria, M. Tabasso, "Measure of Porosity and mechanical resistance in order to evaluate the state of deterioration of some stones", Deterioration and Protection of Stone Monuments, International Symposium, Paris, 5-9 juin 1978 (Paris: UNESCO RILEM, n.d.), 2.1.

8. C. A. Price, "The Consolidation of limestone using a lime poultice and limewater", Adhesives and consolidants, preprints of the contributions to the Paris Congress, 2-8 September 1984, (London: IIC, 1984), p. 160-162.

SUMMARY

The calcareous rocks and monuments made of this material are being weathered since long. Very little attention has been given to preserve these rocks. A few methods like applying Organic polymers have been studied but they are found to be less effective. In this paper, discussion regarding weathering process of the rocks by different agents particularly bio-degradation has been discussed and a new method i.e., applying Inorganic polymer coatings has been suggested. The calcareous materials treated with Inorganic polymers have been tested against bio-degradation and different weathering agents. It has been observed that the Inorganic polymers are quite effective to arrest the further deterioration.

DETERIORATION AND CONSERVATION OF CALCAREOUS STONES

M.C. Ganorkar, T.A. Sreenivasa Rao and M. Bhaskar Reddy
The Birla Institute of Scientific Research
Asmangadh Palace, Malakpet
Hyderabad - 500 036
India

Introduction

Calcareous stones exposed to the environment are subjected to a wide variety of stressing agents such as wind, solar radiation, temperature, Biological species, acid rains, dew, snow, sleet, fog and aerosols. It is a well known fact that rocks exposed to these weathering agents deteriorate very fast. Attempts have been made to stop this deterioration by applying coatings of Organic compounds like epoxy resins, Silicone resins and methacrylates. The weathering of the calcareous stones takes place first by the loosening of the surface structure and then the deterioration of the internal structure.

The literature survey shows that weathering process of the calcareous stones by the atmospheric Sulphurdioxide gas, Soluble salts, rain water and biodeterioration consists the following points:

1. The surface of the stone will be attacked first. Sulphur dioxide in the humid conditions will attack the surface layer leading to the formation of gypsum (1).

2. The gypsum thus formed on the rock surface will combine with the soluble salts present in the rock to accelerate the deterioration process by the reported mechanism (2).

3. In Industrial atmosphere, the rain water has a pH variance of 4.5 to 6.3. The Carbon dioxide present in the atmosphere reacts with Calcium Carbonate in humid conditions and releases Calcium ions (3).

4. The pore structure of the rock will accumulate water and salts due to the change of the atmospheric cycles. This will form bed for the growing of the fungus on the rock surface. Weathered zones will be more susceptible to the fungal attack (4).

Considering all the above factors the biodeterioration of the calcareous stone will be predominant in the samples having more weathered surface. Identification of the weathered sample which is first attacked by the biological species is important.

Bio-deterioration of the rocks is mentioned by the several authors (5,6). Acid excretions by the fungus on the rock will form soluble metal chelates which are the nutrients for the growth of the fungus. The excess of these soluble chelates are washed away by rain water.

The release of metal ions by calcareous stones and cleavage of the rock structure by the excreted acid is not well studied. In this paper we have discussed about the release of soluble chelates by the fungal attack.

In order to stop the weathering of the rocks, it is necessary to protect the surface of the rock by the external material which should be resistant to rainwater, air pollutants, fungi and bacteria. Organic compounds have been tried, but proved to be less effective. A new process that is formation of a layer of inorganic polymer on the surface of rocks is being studied and the results obtained shows that complex formation can stop the weathering process. It is well known that calcium ions react with number of Organic compounds (ligands) and form complex species. These complex species of calcium are found to be very resistant to all types of pollutants and fungal and bacterial attacks.

Materials and Methods

Five limestone and five marble samples of 200 mesh were taken up for bio-deterioration.

Surface area analysis was carried out by the rapid surface area analyser (micromeritics 2200). Soluble sulphates determined by measuring the turbidity of barium sulphate suspension by spectrophotometer (ECIL GS 866 C).

Infrared spectrophotometer (PE 781 model) was used to carry out the spectral analysis. Atomic absorption spectrophotometer (perkinelmer 2380) used for metal estimations.

Specifically designed reflectance IR spectrophotometer fabricated by National Remote Sensing Agency, India was used for testing of the polymeric coatings.

Results and Discussion:

1. To estimate the extent of damage to the surface

The extent of damage done to the stone at the molecular level was given by surface area analysis. Sulphate ion estimation gives the formation of gypsum. Table-1 gives the specific surface area (SSA) values, Surface area of the sample per gram and percentage of Sulphate ions.

Table - 1 Values of specific Surface area and Sulphate ion concentration

LIME STONE			MARBLE		
S.No.	% SO_4^{2-}	S S A	S.No.	% SO_4^{2-}	S S A
L ₁	0.9606	6.244	M ₁	0.7065	0.419
L ₂	0.6616	2.318	M ₂	ND	ND
L ₃	0.4716	2.025	M ₃	ND	ND
L ₄	ND	ND	M ₄	ND	ND
L ₅	ND	ND	M ₅	ND	ND

ND = Not detectable

The sulphate ion concentration is more in L₁ indicating the weathering. SSA values also indicate the rock surface became more porous. The samples L₂ and L₃ are less weathered when compared to L₁. Similarly M₂ having more Sulphate ion concentration and hence more SSA weathered to a large extent. The samples L₄, M₂, M₃, M₄ and M₅ contains a little amount of Sulphate ions do not undergone deterioration at all. L₁ and M₁ having more weathered surfaces have been taken up for the bio-deterioration studies.

2. Bio-deterioration

It has been reported in the literature that penicillium fungus excretions mainly consists of citric acid (7). When this fungus grows on the rock it is difficult to detect where deterioration has occurred. So we have followed an indirect method i.e., the calcareous stones were treated with different concentrations of citric acid and the pH of the solution monitored at different time intervals. It has been observed that pH of the solution increases with the time interval indicating the formation and solubilization of metal chelates. These pH changes are given in Table - 2.

The values shown in the Table-2 shows that the concentration range (0.0001 to 0.0009M) the pH variation reached the maximum value by two weeks and then it becomes constant. At the concentration range (0.001 to 0.03M) pH variation goes on increasing till 4 weeks. At the concentration range (0.05 to 0.1M) pH does not show any appreciable change. This may be because of the high concentration of the acid which destroys the metal chelates formed immediately.

The surface area of the samples at the concentration range (0.01 to 0.1M) increases suggesting inclusion of water molecules deep inside the crystal structure, suggesting that at this concentration, the surface of the rock is undergoing some change.

Table - 2 pH of the solutions

S. No.	Concentration of the acid	pH of the acid	pH of acid + sample	WEEKS			
				1	2	3	4
1	0.0001	4.8	8.6	8.1	8.1	8.1	8.1
2	0.0003	4.1	6.9	8.0	8.0	8.0	8.0
3	0.0005	3.8	5.4	7.6	7.6	7.7	7.9
4	0.0007	3.7	5.1	7.6	7.9	8.0	8.0
5	0.0009	3.7	4.8	7.4	7.8	7.9	8.1
6	0.001	3.6	5.0	7.5	7.7	7.9	8.0
7	0.003	3.2	3.8	6.4	6.8	7.4	7.9
8	0.005	3.1	3.9	5.0	5.5	7.5	8.1
9	0.007	3.0	3.6	4.8	5.5	7.5	8.0
10	0.01	3.0	3.5	4.7	5.0	7.3	8.3
11	0.03	2.9	3.4	4.6	5.6	6.6	7.6
12	0.05	2.6	3.4	3.6	3.6	3.6	3.6
13	0.07	2.5	3.0	3.1	3.2	3.2	3.2
14	0.09	2.4	2.7	3.0	3.0	3.0	3.0
15	0.10	2.4	2.6	2.6	2.6	2.6	2.6

Table - 3 Release of metal chelates from L₁ by acid attack

S. No.	Concentration of the acid (M)	% Ca	% Fe	% Al	% Si
1	0.0001	0.13	N D	N D	N D
2	0.0003	0.35	N D	N D	N D
3	0.0005	0.14	N D	N D	N D
4	0.0007	0.22	N D	N D	0.10
5	0.0009	0.23	N D	N D	0.12
6	0.001	0.30	N D	N D	0.13
7	0.003	0.27	N D	N D	0.135
8	0.005	0.46	N D	N D	0.14
9	0.007	0.63	N D	N D	0.25
10	0.01	1.06	0.016	N D	0.27
11	0.03	2.5	0.065	N D	0.28
12	0.05	2.9	0.16	0.2	0.50
13	0.07	3.0	0.15	0.23	0.61
14	0.09	3.5	0.16	0.70	0.63
15	0.1	3.73	0.18	1.304	0.65

After 4 weeks, solutions were filtered and the residues were washed with distilled water. The filterates were collected and used for the estimation of Ca, Si, Fe and Al. Values are given in Table-3. The residues were dried in vaccum and used for IR studies.

As the concentration of the acid increases the release of Calcium ions increases. At the concentration range of (0.0001 to 0.007M) release of Siliconions is less when compared to Calcium ions and there is no release of Iron and Aluminium ions. It is interesting to note that at the concentration range of (0.01 to 0.03M) the

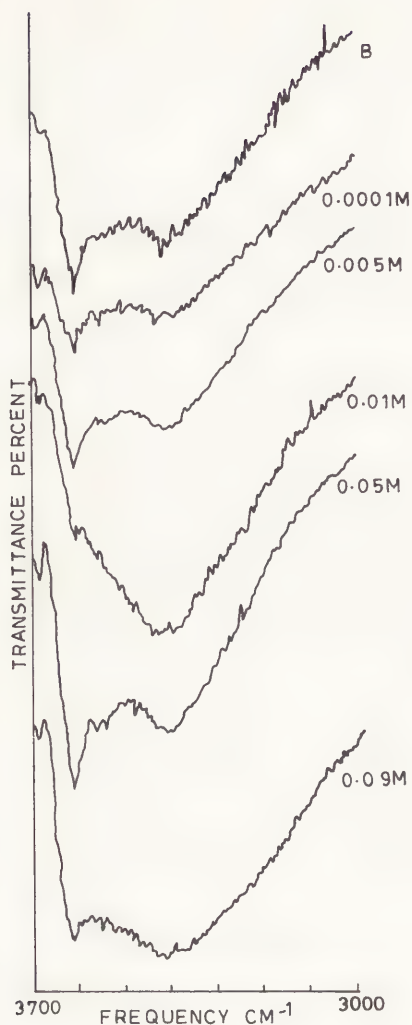
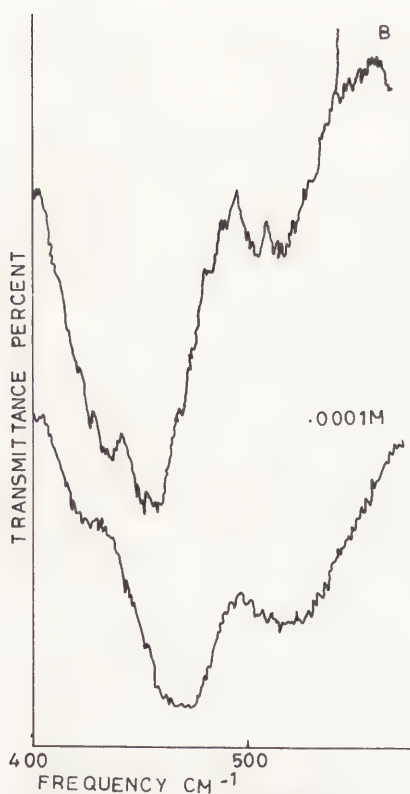
**Fig. 1**

FIG 1, FIG 2, FIG 3 gives the altered I.R. spectra.

**Fig. 3**

concentration of Calcium ions suddenly increases and the release of Iron ions also noted. At the concentration range of (0.05 to 0.1M) the release of Aluminium ions also occurs due to the loosening of the crystal structure.

The release of Calcium ions and Silicon ions initially and later on Iron ions and Aluminium ions suggest that as the concentration of the acid increases the rock surface is undergoing a change. Appearance of Aluminium ions in the solution indicate that inner surface is also being effected.

IR Studies

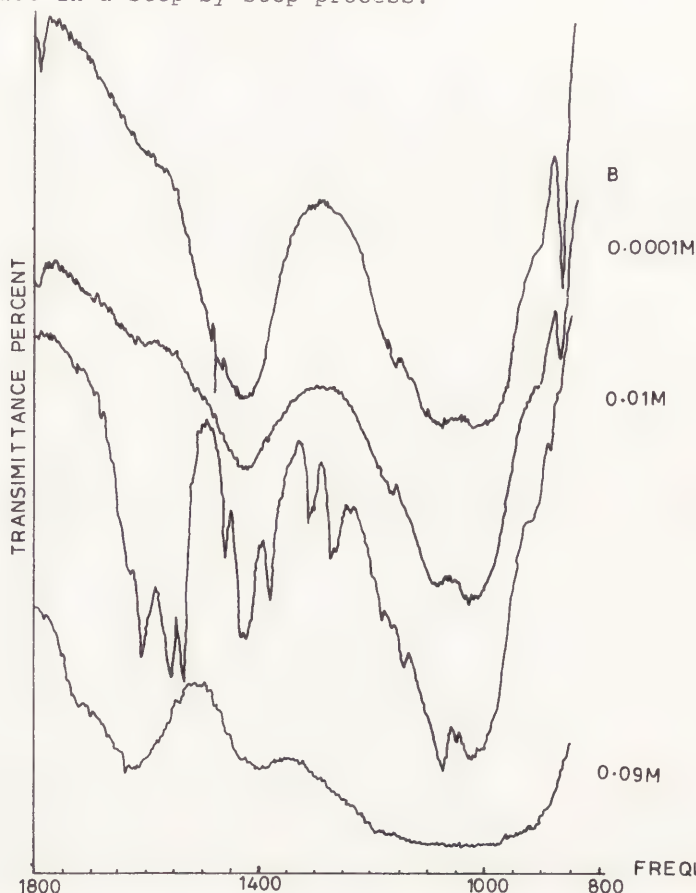
The IR spectra of the residues of the 15 samples have been recorded

Fig 1 and 2 give IR spectra of L_1 treated with various concentration of the acid. From the IR studies it has been observed that at the concentration 0.01M a big trough appears in the region of 3400 to 3600 cm^{-1} indicating the presence of water of crystallisation. The other interesting point that has been observed was that there is a regular decrease of the carbonate peak in the region of 1430 - 1500 cm^{-1} and then sudden break-up of this peak into three bands appearing at 1610, 1590 and 1430 cm^{-1} . From these observations, i.e., appearance of a big trough and change in carbonate peak, it was concluded that at the concentration 0.01M structural changes were taking place.

A peak in the region of 1030 - 1100 cm^{-1} is observed, assigned to Si-O vibrations, was getting widened at the concentration of 0.05M. This change was attributed to the disruption of ordered crystalline structure of silicate minerals.

The metal oxygen bonds observed in the blank, in the region of 600 - 400 cm^{-1} are quite sharp, in the treated materials these frequencies are appearing as broad bands, this change in intensity of the bands may be due to the weakening of metal-oxygen bonds. Fig 3.

The above data showed that fungal attack deteriorate the rock surface in a step by step process.

**Fig. 2**

3 Chemical Inhibitors

It has been reported that calcareous stones are susceptible to fungal attack (6). In order to stop this type of degradation inhibitors have been mentioned in the literature (8).

We are here reporting the inhibitor action of some of the Inorganic polymer coatings on the calcareous stones. Organic compounds (ligands) which form polymeric coatings were mentioned in Table-4.

Table - 4 Organic compounds (ligands) which form polymeric coatings

Sl.No.	Chemical Name	Notation	Concentration
1	Ethylene Diamine	E D A	0.05 M
2	Formaldehyde	F A	"
3	Acetaldehyde	A A	"
4	Semicarbezide Hydrochloride	S C H	"
5	Thio Salicylic Acid	T S A	"
6	Thio Barbituric Acid	T B A	"
7	N ¹ -Naphthyl ethylene diamine dihydrochloride	N ¹ E D	"
8	2-carboxy thio ethanolamine hydrochloride	T E A H	"
9	2-carboxy 5-Bromo thioethonal emino thio urea	B T U	"
10	Ortho-Phenanthraniline Diamine	O P D A	"
11	Thiosemicarbazide	T S C	"
12	Benzotriazole	B T A	"

Table - 5 Complexing ability and percentage inhibition

Sl. No.	L ₁ + citric acid (0.0001M) % Ca	Ligand	L ₁ + ligand % Ca	Complex of the ligand + citric acid (0.0001M) % Ca	Percentage inhibition
1	0.13	E D A	0.16	0.10	24
2	"	F A	0.18	0.09	30
3	"	A A	0.14	0.10	24
4	"	S C H	0.10	0.04	70
5	"	T S A	1.08	0.08	39
6	"	T B A	0.58	0.04	70
7	"	N ¹ E D	0.18	0.02	84
8	"	T E A H	0.12	0.04	70
9	"	B T U	0.90	0.07	46
10	"	O P D A	0.08	0.02	84
11	"	T S C	0.95	0.09	30
12	"	B T A	0.06	0.01	92

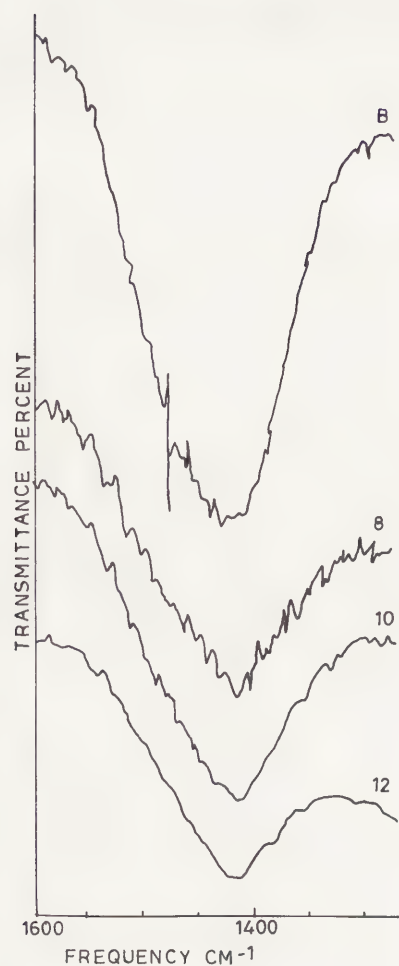


FIG 4 Reduction of carbonate peak due to complexation.

For complex formation study sample L₁ was used. Three types of experiments have been carried out 1. L₁ + citric acid (0.0001M) 2. L₁ + ligand 3. Complex of the ligand + citric acid (0.0001M) and the release of Calcium ions in all these experiments was presented in Table-5.

The data reveals that SCH, TBA, N¹ED, BTA form insoluble complex layer on the samples which is resistant to citric acid. In case of other ligands complex formation is there but these complexes are soluble in water giving more amount of Calcium ion content. The best inhibitor was found to be BTA.

The formation of the complex is further confirmed by IR studies Fig-4, from IR spectra it has been noticed that the carbonate peak is reduced in all but the reduction in the case of BTA complex is maximum, indicating that the formation of stable complex layer on the surface.

The efficiency of these complex coatings is also tested by growing penicillium fungi on the marble samples (4" dia). Fig - 5 gives the growth of the fungi on the surface of the sample, after 15 days incubation at 25°C. The samples were taken out and washed with water. The complex coating on the marble samples remains intact.

The above data shows that biodeterioration can be stopped effectively by inorganic polymers.

We have tried the efficiency of these inhibitors for the air pollution also by using specifically designed reflectance IR spectrophotometer Fig - 6.

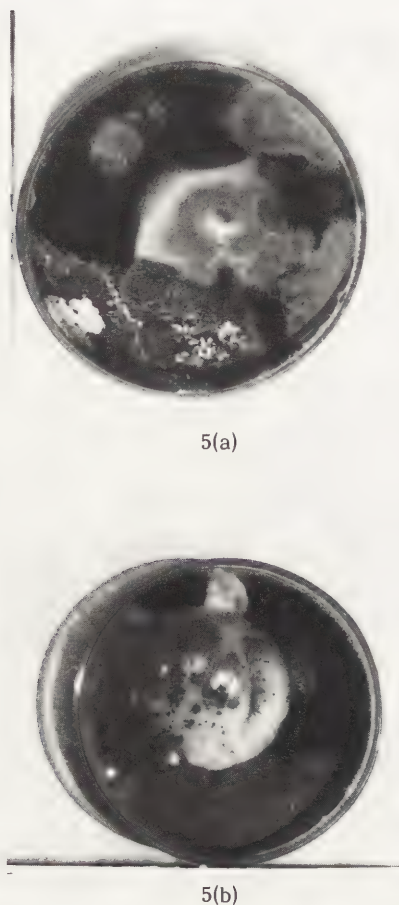
Marble samples (4" dia) have been coated with all the ligand solutions and washed with water and their reflectance values were in Table - 6.

Table - 6 Stability of the complex coatings by the ligands on the marble.

Sl. No.	Initial reading	Chemical applied (ligand)	After coating with the ligand	After washing with water	Colour of the surface
1	94	E D A	44	97	White
2	94	F A	80	92	"
3	74	A A	56	70	"
4	86	S C H	77	77	"
5	92	T S A	80	92	Yellow
6	80	T B A	69	69	Light yellow
7	94	N ¹ E D	80	80	Light brown
8	90	T E A H	75	89	Yellow
9	80	B T U	65	75	"
10	94	O P D A	44	44	Snuff color
11	90	T S C	55	89	White
12	82	B T A	14	14	"

Table - 6 shows that in this case also the carbonate peak is reduced to maximum with BTA. This shows that BTA is a better complexing agent when compared to N¹ED, TBA, SCH. In support of our data obtained by the new reflectance IR instrument, reflectance spectra on the other instrument was also recorded. The graphs obtained are given in Fig - 7.

From these figures it can be concluded that the spectra obtained on the two instruments were very similar.



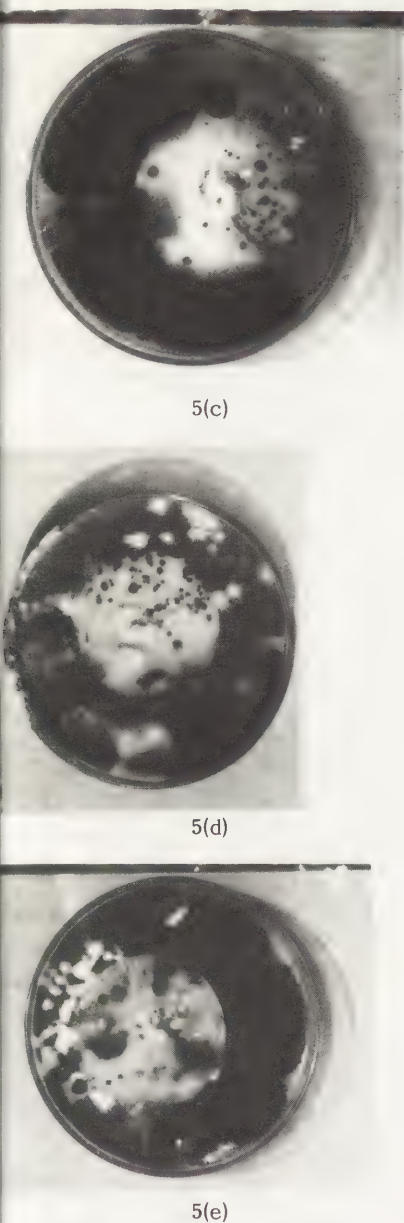


FIG 5 Pencillium fungi grown on the samples 5(a) Blank, 5(b) SCH, 5(c) N¹ED, 5(d) TBA, 5(e) BTA,



FIG 6 Reflectance IR spectro - photometer

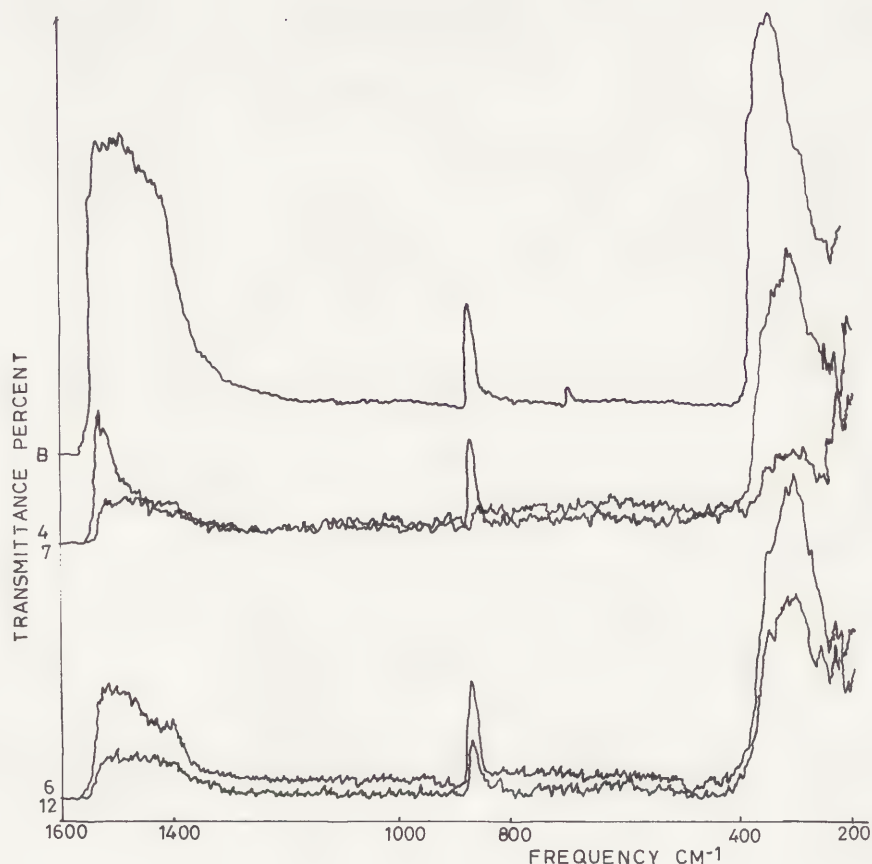


FIG 7 Reflectance infrared spectra of marble samples coated with the inhibitors

Samples coated with BTA, N¹ED, TBA, SCH were exposed to the ambient atmospheric Sulphur dioxide of concentration 80 ppm with 43 percentage of relative humidity and time of exposure 4 weeks. Table-7 gives the stability of these coatings for atmospheric pollutants.

Table - 7 Stability of the complex coatings in SO₂ atmosphere

Sl. No.	Sample No.	Initial reading	After exposure to SO ₂ gas	After washing with water
1	4	77	77	77
2	6	69	67	69
3	7	80	71	80
4	12	14	10	14

The above data indicate that all the four ligands can be used as bio-deterioration inhibitor agents and as protective coatings to the SO₂ atmosphere.

Acknowledgements :

The author wish to thank Prof. Manohara Chari, Botany Department, Osmania University, Hyderabad, for his cooperation in testing Biological activity.

REFERENCE:

- 1 A recent survey on air pollution in Venice in relation to the deterioration of marble and stone. *Lithoclastia* Vol. 2, Vascofacina, 1976.
- 2 Decay and preservation of stone (book). Editor: E. Winkler, Published by Geological Society of America pp.37.
- 3 Reactivity of treated and untreated marble in carbon dioxide atmosphere. K.L. Gouri et al, *Transactions of the Kentucky Academy of Science* Vol. 38, No. 1 to 2, March, 1977.
- 4 Growth control of Algae and Cyano bacteria on Historical Monuments by mobile UV unit. J.M. Vander Molen et al, *Studies in Conservation*, Vol. 25, pp. 71, 1980.
- 5 Fungal attack on rock; solubilization and altered infra-red spectra. Melvin P. Silvderman et al., *Science*, Vol. 169, pp. 985 - 987, September, 1970.
- 6 Mechanisms of the microbial degradation of minerals in sand stone monuments, Mediveal Frescoes and Plaster. F.E.W. Eckhardt, V International congress on deterioration & Conservation of stone Lausanne pp. 643 - 652, October, 1985.
- 7 The release of metallic and Silicate ions from minerals, rocks and soil by fungal activity. Moria E. Henderson, *Journal of Soil Science*, Vol. 14, No. 2, pp. 237-245, 1963.
- 8 A new method for assessing the resistance of stone to algal dis-figurement and the efficiency of chemical inhibitors. C. Grant et al., V International congress on deterioration and Conservation of stone. Lausanne, pp. 663-674, October, 1985.

SUMMARY

The stone objects collection of Gołuchów Castle Museum contains several hundreds of pieces of figurative, bas-reliefs, architectural and ornamental sculpture. Many original masterpieces were purchased in the second half of XIX cent. from France, Italy and Spain. Some pieces have been found in place, and a number has been made as copies of authentic pieces. Nearly all objects of marble, sandstone, limestone, stucco and terra cotta are firmly built into outer and inner walls of the castle. Since 1962 the collection has been undergoing treatment consisting mainly in cleaning and desalting; there were applied several methods of dry and wet cleaning and moist paper pulp method of desalting. Care should be taken to see that the dust and dirt are not let into the pores of the stone. Some protective measures have been taken against deep moistening, algal-lichens and moss vegetation.



THE METHODOLOGY FOR THE CLEANING AND DESALTING OF STONE OBJECTS IN GOŁUCHÓW CASTLE MUSEUM

Janusz Lehmann
Muzeum Narodowe
61-745 Poznań, Poland
Al. Marcinkowskiego 9

Introduction.

The Castle of Gołuchów is one of the best preserved and most representative of the Polish residential castles. It was constructed in 1560 and extended in the beginning of XVII century by an Silesian architect Anthony Lamsit, as a residence of voivodes of Kalisz from family Leszczyński, of which one member - Stanisław /1677-1766/ was King of Poland /1703-1709 and 1733 - 1735/, Grand Duke of Lorraine /1736-1766/ and father in law of King of France - Louis XV. In the beginning of XIX century the castle was ruined. In 1872-1885 reconstructed and partly rebuilt in the style of French renaissance on the initiative of Isabelle Działyńska, born Czartoryska, after the idea of romantic restoration partly drafted by Eugene E. Viollet le Duc, by collaboration of Sigismund Gorgolewski and Maurice Ouradou, for a museum housing fine-art collections of the family Czartoryski. The collections have been scattered during the War 1939-1945, and only a minor part got back in 1956. Since 1952 Gołuchów Castle belongs to National Museum Poznań as a department.

Princess Isabelle Czartoryska-Działyńska assembled in years 1872-1885 a large number of pieces of figurative and decorative stone sculpture dating from classic antiquity to renaissance times. The collection contains now many masterpieces of figurative sculptures, bas-reliefs, mosaics, inscriptional and heraldry cartouches, porticos, portals, window-heads, lintels, decorated chimneys, columns, pilasters, inlays, balustrades, cornices etc., of marble, sandstone, limestone, stucco and terra cotta. Some pieces have been brought out in place from the ruins and a part are copies made of authentic pieces. There are objects of special interest purchased in France, Italy and Spain, and among others: rich decorated renaissance portico from Bargello in Florence, 7 renaissance stone medallions with heads of Roman Emperors from Tourrain Castle, great mosaic medallion with head of goddess Roma VI cent., Naples; great mosaic frieze and 9 red marble portals from Sienna, lintels from Chartres and Limoges Cathedrals, the main portal, 2 statues of Our Lady with Child and 2 chimneys from Florence, statues, medallions, chimneys, portals etc. from Venice, Seville, Rome. Nearly all stone objects are composed within structure or decoration of the castle and built firmly into the outer as well as into inner walls up to it. Therefore the collection saved unharmed through the war.

In the museum the first essential for good conservation is to keep objects free from dust and to limit or to avoid water penetration or condensation of moisture into the pores of the stone. Surfaces should be kept free from dust by frequent, periodic cleaning, for which purpose a clean brush with long, soft hairs, a clean feather duster or a vacuum cleaner /for sound exhibits only/ should be used. Objects should always be cleaned at first from top to bottom, taking care not to taken away loose or delicate fragments of decoration. Vacuum cleaner should be outfitted with appropriate set of nozzles and soft brushes. Cloth should never be used since it stuffs the dust into pores of the stone and fills the hollows with dirt.

Even so, there comes a time when applying of wet cleaning methods is necessary, particularly in the case of dense, polished, light coloured and gilded or polychrome stones, like marbles, granites, stuccos. For porous kinds of stone like sandstones or limestones normal wet cleaning or washing methods should not be applied, since they introduce water and dirt into deeper zones of the stone. In that case special methods of wet cleaning must be applied.

Crystallization, hydration and hydrolysis of salts in stonework is constantly recurring problem, especially in the case of excavated stones brought into an interior as well as in the case of ancient stone objects from interiors transferred and exposed to the humid and polluted atmosphere on the outside display. In Gołuchów Castle we have both categories of stone objects liable to decay by salts. There are some Cyprian inscription plates from excavations which are built into inner wall of the castle and many stone architectural sculptures exposed on the outside to the seasonally polluted atmosphere, because there are local source of

air pollution resulting from the coal heating of the castle.

Exposition in an interior conditions has of course arrested the movement of salts and preserved the stone objects from excavations. But this solution is not possible for objects on the outside and therefore it is the preferable alternative to extract salts from the stones. For the long run it is the more certain method of ensuring preservation.

Organic growth on stone visible to the naked eye is usually green or greyish brown and takes place at certain periods of the year in lower parts of the inner courtyard under the shadow, where is lack of ventilation. It consists of algae, moss and lichens. Great care must be taken in removing the roots of mosses and lichens and in washing the stone with the toxic solution which also immunizes stone against the repeated attack of bryophyta.

Cleaning.

- Every day maintenance and dry cleaning.



The first essential for good maintenance of stone exhibits in the museum is to keep objects free from dust. The chief hazards here are the deposition of dust containing carbon and dirty matter. The effect is of course not as severe under indoor conditions on display or in storage as with exterior exposition of stone. The damage may occur in the form of unpleasant staining resulting from the combined effects of dust deposition and wrong cleaning which works in rubbing it into deeper zones of the stone.

In the Gołuchów Castle Museum stone objects in storage are protected against dust by covering them with slip covers made of thin, soft, white cotton flannel. The exhibits on display are kept free from dust by periodical, normally daily cleaning. Sound objects are cleaned every day, before the opening of museum for visitors, by means of vacuum cleaners with special nozzles and soft brushes. Care should be taken to see the brushes are clean.

Polychrome, gilt and fragile stone objects are cleaned periodically, for which purpose a clean brush, with long, soft hairs is used. Objects always are brushed from top to bottom, taking care not to remove loose or delicate elements of decoration or weakened stone surface. Cloths are not to use even to clean objects in outside exposition because they can rub dirt into pores and fill hollows with it.

- Washing and wet cleaning.

Before washing or wet cleaning each stone object is first accurately dry dusted and cleaned. Washing with water may be desirable and necessary in the case of sound, compact, nonporous stone with smooth or polished, light coloured stones like marble, alabaster, granite, gabbro etc., and when dirt is excessive because lack of regular maintenance. For this purpose we use a 1 - 3 per cent solution of good quality, non-ionic detergent in distilled water. The detergent solution is prepared in a plastic vessel. Care should be taken that the tap water for rinsing is not ferruginous and hard, and the detergent solution comes not in contact with metallic iron, especially in washing white marble. The object is washed from top to bottom /after dusting/ with a soft brush or shaving brush - so that dirty water cannot remain for long in hollows of the carving. After washing the object is rinsed with de-ionized tap water and mopped with a soft, clean, white flannel.

Water solution of detergent can be used in cleaning when it is certain that the stone does not absorb water. Care should be taken because there are some sorts of porous stone which seem to be compact.

Porous limestone and sandstone, sound and plain objects in Gołuchów Castle Museum are wet cleaned. The object is first accurately dry dusted. It is then entirely covered with a thick layer of dense paste which consists of 10-12 per cent methyl-cellulose or polyvinyl alcohol, 3-5% glycerine, 2-3 % non-ionic detergent of good quality and 0,1 % zinc silicofluoride and 80-85% of distilled water. Methyl cellulose or polyvinyl alcohol allow to swell for about 12 hours in a whole quantity of water, then add non-ionic detergent, glycerine and zinc silicofluoride, mix and sift.

The dense paste is adsorbed by the surface of stone, catches of dirt particles and dissolves soluble salts and other dissolving matters in it. As water evaporates from the paste, the dirt and soluble matters migrate from the surface of stone into the paste.



The paste may be allowed to remain in position on the stone for some period depending on thickness of layer, room temperature and humidity of the air, for some period from one to three weeks. Then the paste becomes dry and flexible film is formed from it. It is to take away before the complete hardening. The hardening is retarded by the addition of glycerine.

The operation is repeated until the stone is perfectly clean. Finally the object is desalted by covering with moist paper pulp, in order to remove the remained traces of detergent, glycerine, methyl cellulose or polyvinyl alcohol and other soluble matters from the stone. The operation is described in next section "Removing of soluble salts."

- Removal of stains.

The common staining ingredients of dust can be removed by dusting, washing or wet cleaning, but when the stain is localized and highly coloured, it is usually best to determine the nature of the stain and to remove it by means of selective solvents suitably prepared. In Góluchoń we have removed stains from stone objects after dusting, but before wet cleaning.

Preliminary tests are always made in order to determine the nature of stains and to check the action of solvents or reagents by applying them locally on a cotton wool wrapped round a toothpick. In the same way small stains are removed from the surface of compact and resistant kinds of stone.

A common type of staining is that, due to paints. A thick blob of paint should be carefully scraped without damaging the stone. Residue after scraping is treated with suitable solvent; for water paints the suitable solvent is water to which some ammonia has been added. For oil paints we use a mixture 1 : 1 : 1 of turpentine, ammonia and triethylamine or morpholine. If we need the solvent in the pasty condition, we make a mixture with polyethylene glycol / PEG 4000 / as thickening agent. Such paste is used to remove stains from inconvenient vertical or upside down surfaces and from porous sorts of stone, where thin solvent could diffuse stain around and introduce coloration deeper into pores of the stone. In the same way we remove bituminous tar stains using a mixture 1 : 1 : 1 of benzene, turpentine and methanol with PEG addition to thicken the solvent if necessary.

Iron, ink and color /e.g. after removing of lichens/ stains defy all solvents and can only be taken away by using appropriate reagents. The problem of removing such stains is further complicated by the fact, that all acidic reagents are able to desintegrate several kinds of stone, especially marbles, limestones, dolomites, alabasters, stuccos etc. Therefore the use of them for removing stains is out of the question. Only neutral and slightly alkaline reagents are permissible, and when are used they should be left for short only in contact with stone and then all traces of them washed off very thoroughly.

Ink and most part of colour stains may be removed by using freshly prepared 3 per cent aqueous solution of chloramin T.

Iron and remaining colour stains which don't disappear when treated with chloramine T may be removed by alternate application of selected reducing, oxydizing and complexing reagents. As complexing reagents we use 5 per cent aqueous solution of complexon 3 / sodium salt of EDTA - $\{Na_2OOCCH_2\}_2NCH_2\}_2$ and-or 5 per cent solution of 8-hydroxyquinoline - C_9H_7ON in the mixture of 1:1 of water and methanol. As reducing reagent sometimes in the case of resistant stains we have used 5 per cent solution of oxalic salt - $NaKC_2O_4$ /sodium-potassium oxalate/ in water. In order to thicken solvent we add some 10 per cent methyl cellulose and 3 per cent glycerine if necessary.

After removing of ink, colour and iron stains by means of reducing or complexing reagents a slight residual coloration may remain. It can respond to the treatment with 5 per cent aqueous solution of hydrogen peroxide - H_2O_2 .

It should be noted, however, that colour ingredients of the stain will certainly have been removed to great extent by the stone if it is possible to eradicate all the staining matter, sometimes the chances of disappearing stains without leaving a trace of coloration are remote indeed, especially on white sorts of stone, and a slight grey or brownish residue can remain. This may be not a serious problem if the colored residue is in an inconspicuous area, but if the remaining trace is a disfigurement it is

better to retouch it with an appropriate watercolor rather than to tire the stone with chemicals.

When smooth or polished surface of stone is blemished locally with an insoluble matter the satisfactory treatment may be to wet the stone and scrape away the deposit by rubbing with a small slip of India-oil stone or fine corundum sliding stone. When applied lightly does not impair the surface of the stone.

Removing of soluble salts.

The combined action of different meteorological, physical and chemical agencies causes direct disintegration known as weathering of rocks and indirect forms of attack - transport of soluble salts and leaching of soluble constituents of stone, growth of microorganisms, cryptogams and vegetable organisms. In certain objects some changes indicating indirect forms of stone decay - transport of soluble salts and biological attack may be observed.

The increase in the content of air pollutants in the atmosphere may considerably affect stone. There are two main kinds of sources of atmospheric pollution - permanent contamination coming from industrial areas, transported along atmospheric fronts on long distances, and seasonal-local which release contaminants into the atmosphere by the combustion of coal and other fuels, as well as by the putrefaction of great masses of organic waste material. The analytical result of this local and imported contaminations may be slight, but because cumulative reaction during long time of airborne contamination on stone could be very considerable. It results mainly in accumulation of soluble salts and in accretion of insoluble incrustations. The removal of soluble salts may be carried out by various methods as immersion in water, forcing water through the stone, treatment with warm water, sealing in the salts and extraction by moist paper pulp.

In Gołuchów Castle Museum we have carried out the extraction of soluble salts applying the method of moist paper pulp for some stone exhibits in in and outside, because they are built firmly in the walls. One of treated objects was bas-relief presenting the "Procession of Bacchus", made of greyish green, glaucolitic sandstone - Florence, XVI century. Two other objects - Cyprian inscription tables are made of white yellowish limestone and built into an inner wall.

Paper pulp was made by soaking and cooking of white, ground sag paper of good quality in distilled water with addition of 1 per cent of glycerine. The object was entirely covered with a thick layer of moist paper pulp. The pulp remained on the stone surface for two weeks till it has been dried, and then it was taken away. Fresh pulp was then applied immediately and operation has been repeated as necessary.

Removal of biological organisms and sterilization.

Lack of air circulation in the lower parts of courtyard in Gołuchów Castle and periodical rain fall are the main reasons for the algal, moss and lichens growth on the surface of walls and sculptures in northern position.

A method that was applied in removing of surface contamination of this vegetation was the use of stripping film. The procedure was elaborated for removing stains from porous sorts of stone, and it consists in applying a viscous solution so compounded that, on drying, it forms a strong and flexible film. When it is peeled off, it takes the cryptogams and their deadened remains with it. In this case we have chosen a thick nitrocellulose solution in a mixture 1 : 1 of ethyl acetate and cyclohexanon with addition of 5 per cent of paraffin oil to prevent to strong adhesion to the surface of stone.

In the case of compact, waterproof stone, organic deposits caused by the growth of cryptogams on the surface of stone in the open have been first softened by means of dilute ammonia / 1 : 20 / in distilled water under a compress on lignin. The compress remains 24 hours and then the deposits are removed by washing with soft brush and deionized, free of iron water.

In order to improve situation we have added 0,1 per cent zinc silicofluoride and 0,5 per cent formalin as sterilizing agents to the wash water.

After complete drying of stone we applied to impregnation of cleaned stone objects the dilute / 2 per cent / solution of silicon resin - Silak M 11 produced by Chemical Factory at Oświęcim-



Poland, in a mixture 2 : 1 of ethyl acetate and methanol, as water repellent agent.

Until recently very little protective treatment, as such, was applied to stone historic and artistic works, but the various restoring processes used, including partly reconstruction of stone, painting and gilding. Only during last decades have methods been devised and applied to arrest or to slow down the deterioration of stone.

The subject of this paper is to present an example of the conservation of stone objects in a more direct sense of the term with the remotest restorers intervention after a backward system of principles.

BIBLIOGRAPHY

- Plenderleith, H.J., The Conservation of Antiquities and Works of Art. London: Oxford University Press, 1957.
- Sneyers, R.V., a. de Henau, P.J., "The conservation of stone". In The Conservation of Cultural Property. Museums and Monuments, vol. XI. Paris: UNESCO, 1968.
- Kodurowa, A., Powiat Pleszewski /Pleszew District/, In Katalog Zabytków Sztuki w Polsce. /The Catalogue of Ancient Art Objects in Poland, vol. V, fasc. 19 / Warszawa, Państwowy Instytut Sztuki, 1959.
- Pajzderski, N., Przewodnik po Muzeum w Gołuchowie. /Guidebook to the Museum in Gołuchów/ Poznań: Sztuka i Artysta, 1929.
- Jakimowicz, T., Zamek Leszczyńskich w Gołuchowie. /Leszczyński's Castle in Gołuchów / In Biuletyn Historii Sztuki. / History of Art Bulletin/ vol. XVII. Warszawa, Państwowy Instytut Sztuki, 1955.
- Lehmann, J., Konserwacja zabytków z kamienia naturalnego. /The conservation of antiquities of natural stone/, Biuletyn CZMiOZ, Warszawa: Ministerstwo Kultury i Sztuki, 31 /1960/.
- Lehmann, J., L'étude des pierres en Pologne. In Colloques sur l'alteration des pierres. Paris: ICOMOS, 1968.
- Lehmann, J., Damage by accumulation of soluble salts in stone work. In Conservation of Stone and Wooden Objects, London: IIC, 1970.
- Lehmann, J., Contribution a l'étude de l'efficacité de la conservation des pierres. Monumentum, vol. IX, Paris: UNESCO, 1973.
- Riederer, J., Bibliographie d. Deutschsprachigen Literatur über Verwitterung u. Konservierung v. Naturstein. Berlin: Deutsche Kunst u. Denkmalpflege, 1973.
- Lehmann, J., Recent experience in conservation of stone objects. Accomplishments of the Working Group Stone. In ICOM - Committee for Conservation, 5th Triennial Meeting. Zagreb, 1978.
- Lehmann, J., Recent experience in conservation of stone objects. Accomplishments of the Working Group Stone. In ICOM - Committee for Conservation, 6th Triennial Meeting. Ottawa, 1981.
- Lewin, S.Z., a. Rock, E., Y., Chemical considerations in the cleaning of stone and masonry. In: The Conservation of Stone I. Bologna: Centro Conservazione Sculture all'Apperto, 1976.
- Lehmann, J., Quelques nouvelles recherches sur le nettoyage et la préservation des sculptures en pierres exposées a l'extérieur en Pologne. In: The Conservation of Stone I. Bologna, Centro Conservazione Sculture all'Apperto, 1976.
- Lehmann, J., The conservation of stone objects in museums- examples and experiences. In: -Case Studies in the Conservation of Stone and Wall Paintings. London: IIC, 1986.
- Marschner, H., Steinhydrophobierung in Denkmalschutz. In: Kolloquium über Steinkonservierung, 9-11. April 1984, Münster. Erlangen: H.J.Oel, Institut f. Werkstoffwissenschaften, 1984.



MARY

conservation of a monument with the large proportions and complex problems of a Roman commemorative arch calls for years of study and experimentation in order to refine the actual intervention techniques.

The intervention on the Arch of Septimius Severus, which began in 1979, involves three distinct phases: the preliminary work (documentation); the work in progress (intervention); the maintenance plan (future care).

THE CONSERVATION INTERVENTION ON THE ARCH OF SEPTIMIUS SEVERUS IN THE ROMAN FORUM

Roberto Nardi

Centro di Conservazione Archeologica (C.C.A.)

Via Zanardelli 16, 00186 Rome, Italy

Methodological Premise

The conservation of a monument with the large proportions and complex problems of a Roman commemorative arch is no easy task. It calls for years of study and experimentation in order to refine the actual intervention techniques.

This is a long process of information-gathering, analysis and comparison, during which the trials carried out on the monument are studied and used to verify the theoretical guidelines of the project.

Well-known techniques will be accepted per se; others will be modified; still others will be discarded. In making these decisions, a primary criterion is to ensure respect for the original surfaces. Yet, given the extent of the surfaces to be conserved, we must also think about the practical advantages of one technique or another.

The end of this preliminary research phase coincides with the moment of greatest analytical and deductive effort. We must draw on accumulated experience, while keeping an eye on the materials and techniques used in previous restorations, and also work with the knowledge we have gained about the ancient materials and techniques of construction and maintenance. Given this background, the actual conservation intervention can begin.

Up to 1979, the Arch of Septimius Severus had never been documented in any technical, graphic sense: in particular, no scale surveys had ever been done; there was no comprehensive photographic documentation; there was no record whatsoever of the state of conservation of the stone surfaces; there was no up-to-date literature available, or at least none of a technico-archaeological nature that would help in understanding the surfaces and structures; the archives yielded little documentation that could be used to deduce, even vaguely, the fate of the monument under various administrations over the past centuries; there was no coherent maintenance plan; even the restorations were episodic events, concentrated in the sixteenth-nineteenth centuries, leaving the monument abandoned (fortunately, I am tempted to say) for the past 50 years.

This is the background to the current intervention, and this is why, in 1979, before beginning any direct conservation work, we decided to fill in some of these innumerable gaps in information. The time involved in this activity, combined with the test results that were accumulating, enabled us to draw up the lines of the subsequent intervention on the stone surfaces. Information of various sorts began to come together and was kept in consideration as choices were made. This, together with information obtained at the same time from other Roman stone monuments, helped to establish the definitive guidelines of the intervention.

For example:

- a large part of the stone surface is not bare marble, but is covered with one or more superimposed thin layers (up to 14 on the Temple of Hadrian). The coatings are monochrome (from white to tan, and even red ochre - Arches of Septimius Severus and Titus, Temple of Vespasian and Temple of Saturn). They are a mixture of lime and an organic component, and have played, where still present, a very active protective role, preserving even the most subtle signs of the original working of the marble. Thus the conclusion: these coatings are not "dirt" or "products of alteration of the marble"; they are not "damaging" -- to the contrary, they conserve the surface and thus should not be removed. Cleaning will stop at the level of the outermost layer, and techniques will also be chosen to respect these layers [1];

- the monument was predisposed to receive, and did receive, maintenance treatments; perhaps some of the layers mentioned above are archaeological reminiscences of this activity. A system of internal stairs and rooms, connected with external cornices that could be walked on, made it possible to reach the upper external surfaces of the monument without erecting scaffolding. Thus the conclusion: maintenance is not only an indispensable conservation practice, but also a philological restatement of the ancient idea of the project;



Arch of Septimius Severus.

- changes in the original system of rainwater guttering (cornices and eaves), due to the loss of portions of the stone surface, cause water to flow down over the marble. This impedes the formation of "black crusts", but induces a very active form of deterioration of the surfaces, with continual loss of original material. Thus the conclusion: in the topography of surface deterioration, the "black crust" areas correspond to a lesser degree of deterioration than many of the "apparently clean" areas. The latter, in fact, when they are found beneath cornices and eaves, may indicate overlying lacunae, which should be filled in order to reinstate the lines of the "drip course";

- the cement that was used for stuccoing during previous restorations, and lavishly applied to overlap the healthy marble, is a strong activator of chemical and physical decay. Chemically, it exports soluble salts, which migrate and crystallize in the marble, causing disintegration even at depth. Physically, its greater hardness with respect to the stone places the stone under tensions that in the long run lead to cracks and detachment. Removal of the cement also leads to breaks and loss of marble. Colonies of algae also develop along with the cement, even in apparent absence of light. Thus the conclusion: not only should cement no longer be used, but it should also be removed with great care where present, in order to limit damage as much as possible. Leaving it in place would signify keeping active sources of deterioration on the stone surfaces;

- given the environmental conditions and the condition of the stone on the Arch of Septimius Severus, the use of Paraloid (B72) as a preconsolidant (in varying proportions, 1.5-3% in trichloroethane, applied with a brush to saturation in different areas and at different times) causes the treated area to take on a greyish tone, even after a few months (2-3). The coloration tends to become darker and, even after 12 months, becomes irreversible, at least the part absorbed in depth. Other resins, acrylic or acrylo-siliconic, and even some ethyl silicates begin to show signs of unreliability [2]. Thus the conclusion: Paraloid should not be used extensively in preconsolidation or consolidation. Rather, given that the cleaning is done principally with "wet" systems, hydraulic consolidation techniques should be refined;

- epoxy and silicone resins used for puttying have been found to be irreversible (as on the Antonine Column and the Arch of Constantine), too hard with respect to the original surfaces, and incompatible in terms of physical characteristics. Thus the conclusion: materials to be used for puttying and micro-puttying should be similar or at least compatible in chemico-physical behavior to the stone support. For instance, their mechanical resistance must be equal to, or less than the marble's; their permeability must be equal to, or greater than the marble's. They themselves should be the new "weak point" of the surface, the preferential place for deterioration to occur, and not the source of new tensions and stress;

- surface protection cannot be relegated to a miraculous product that is reversible, stable, transparent, water-repellent, inert with respect to the support, long-lasting, and inexpensive, because such a product does not yet exist (at least not for monuments). Thus we must make compromises, giving way on the points that are less dangerous for the monument but never forgetting the conditions of absolute security the ancient surfaces require. Thus the conclusion: the protective coating can be inert with respect to the support, partially reversible, partially transparent, but it must act as a sacrificial layer that will dissolve in time in contact with the agents of decay [3]. It will decay itself, dissolving without interfering with the support, which is thus "exonerated" from the task of exchange with the environment. Durability is of relative importance: when the sacrificial layer is worn out, it will be replaced. This could be an advantageous price to pay for the conservation of a monument. Lacking a solution of this kind, given the current state of the art, it is preferable to return the surfaces to exposure to environmental agents without applying any of the "classical products" available to us today;

- maintenance is the true keystone in the conservation of monuments: the first work to be done lies in the cultural education of administrators. The monumental heritage is not a fixed income drawn from unlimited riches, but an inheritance that requires serious responsibility, both economic and cultural. Thus the conclusion: the conservation intervention will have a positive outcome only if it is followed by a simple, inexpensive

and efficacious maintenance plan. Lacking this, the intervention now being carried out will be merely the last stop-gap measure granted to us in the monument's 2000-year history;

- the monument was constructed and in part maintained with techniques and materials that have proved to be stable and efficacious over the course of two millennia. Thus the conclusion: never lose sight of the simple materials and techniques of which the monument itself is composed and with which it was built. These must be studied and reintegrated into our professional heritage, and re-proposed whenever we cannot do otherwise. Only in a few exceptional cases should we resort to exceptional techniques and materials that are incompatible with the monument; simple techniques that are closest to normal building maintenance should always be given priority. Thus, simple interventions with simple materials, following the principle of the least intervention possible.

The conservation process

The Arch of Septimius Severus in the Roman Forum (photo 1) was constructed in A.D. 203 with proconessian marble over a structural core of travertine; the top storey is supported by a brickwork vault. Given its location and the grandeur of its structure, the arch has participated as spectator and protagonist in all the events that, in the history of the past 17 centuries, have characterized the life of the piazza of the Republican Forum/Campo Vaccino/Roman Forum.

This historic patrimony has survived to our day through documentary and iconographic evidence, but above all in the surfaces of the monument itself. There are innumerable traces on the marble: these provide precious information but have also damaged the surface integrity.

The monument's life is marked by periods of abandonment alternating with phases of re-use (in the Middle Ages it was turned into a fortress), infrequent restoration interventions and equally rare programs of study. We know of structural restorations in the sixteenth century when the mediaeval superstructures were also demolished. Other major interventions were in 1832, with the insertion of iron rods in areas considered unsafe, and in 1903 with a general structural overhaul of the monument.

Apart from rare cases in the Renaissance and the middle of this century, which offered little in the way of technical analysis, we can say that the Arch has reached us without the benefit of any scientific and objective observation, including graphic surveys [4].

The innumerable traces on the monument's surfaces, together with what little remains of the original workmanship and image, thus represent a heritage of inestimable value which we have undertaken to conserve; they are the reason for the extreme prudence and respect that has characterized our approach to the intervention from its earliest phases.

The process of conservation of the monument involves three distinct phases: the preliminary work (documentation); the work in progress (intervention); the maintenance plan (future care). In general terms of energy and money expended, the phases work out in the following proportions: 45% - 45% - 10% (diagram 1).

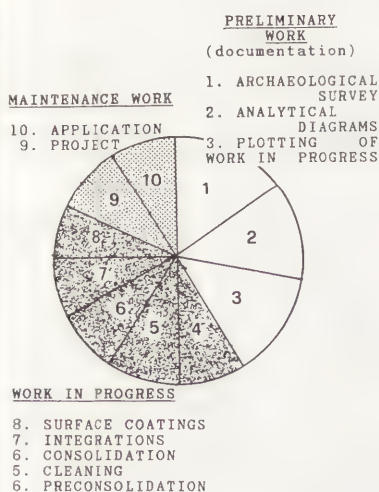
Preliminary work

The aim of the conservation work in progress (note 1) was to protect both the material and the information it bears: thus the documentation phase was extremely important and comprehensive.

The intervention began with a graphic survey of the monument which was done by hand and at a low reduction scale, in order to draw up an initial work plan and to become closely acquainted with the surfaces. This was followed by analytical diagrams which highlighted significant features in the condition of the surfaces.

All the graphic material obtained was computerized in order to provide definitive recording and efficient management of the large amount of data collected. This type of analysis of the surfaces was carried out for a variety of reasons. Primary among these was the desire to leave a detailed report, with topographic indications, of the condition of each portion of the surface from both the historico-archaeological and the conservation viewpoint.

THE CONSERVATION PROCESS



1. The conservation process.



2. Diagram of the state of conservation. Loss of original stone facing the Roman Forum: the loss is great as 90%.

and also to have a firm basis for publishing studies of the monument. The second motivation was to have theoretical models on which to study in detail the mechanisms of decay, the behavior of materials, and the proposed conservation techniques. Furthermore, we wished continually to update, follow and check the condition of the surfaces in relation to the progress of the work, and finally to draw up and manage a detailed maintenance plan for the monument, a natural extension of the immediate intervention. Examples of the practical use of such graphics are as follows:

- the possibility of studying, in a monumental context, the numerous monochrome layers (composed of lime mixed with an organic component) present on the stone surface and especially the possibility of correlating these features with the stratigraphy of the monument's burial;
- the possibility of reconstructing the phases and extent of past restorations that were not otherwise documented;
- the opportunity to quantify the damage suffered by the monument through calculation of areas of loss of the original surfaces. In the case of the side facing the Roman Forum, the loss is as great as 90% (diagram 2);
- the possibility to study the relationships between areas of surface loss, structural alterations, changes in rainwater runoff and the forms of stone decay, with the resulting possibility of getting at the root of the problem by removing the very causes of these forms of decay.

The diagram of the state of conservation is an instrument that constantly follows the restorer on the scaffolding so that he can record, first on paper and then on diskettes, every operation carried out on the monument.

Work in progress

- Preconsolidation

By preconsolidation of the surfaces we mean an initial series of first-aid interventions carried out even before the research phase is transmuted into execution. For a second series of operations, connected to the actual restoration intervention and implemented just before surface cleaning, see the "consolidation" phase below.

The state of decay of the stone surfaces of the Arch of Septimius Severus was such that it was necessary to consolidate and fix the deteriorated and unsafe marble parts prior to any other operation.

The following operations were carried out: consolidation through repeated applications of ethyl silicate, brushed on; fixation using a covering of Japanese paper and Paraloid B72 in trichloroethane in percentages varying from 15% to 20%. While these procedures did function as desired, we found, 24 months later, some unexpected characteristics: the areas treated with ethyl silicate had a tendency to get progressively browner, while the Paraloid when treated with acetone or trichloroethane for removal, would dissolve on the surface but not where the decayed marble had absorbed it in depth. This left the marble filled and stained with a dark grey plastic that was not very reversible.

As mentioned above, these results were unexpected and perhaps they represent an anomalous case due to the particular state of disintegration of the marble and the exposure of the monument. Nonetheless, they were a factor, as we shall see, that had to be borne in mind and that influenced subsequent choices.

Cleaning

For the cleaning, as indeed for the products used and all the other facets of the conservation intervention, we cannot speak of a single system, but rather of one technique prevailing over others that were, however, also employed and useful in particular situations and chosen according to rules dictated by long experimentation and now supported by worksite practice.

During the preliminary study phase, we carried out cleaning tests with methods chosen on the basis of experiments carried out in the course of other interventions or on the basis of information in the literature. Some cleaning techniques were not taken into consideration, for example, sand-blasting or micro-sandblasting, hot or cold water under high pressure, acid or basic substances. The methods considered potentially suitable for the state of the monument were compared according to the criteria and judgements summarized in diagram 3.

	NEBULIZED WATER	NEBULIZED WATER + H ₂ O ₂ + H ₂ SO ₄	AB57	MICRO SANDBLASTER	ELECTRIC MICRODRILL	PNEUMATIC MICRODRILL
AVAILABILITY	GOOD	POOR	FAIR	GOOD	GOOD	FAIR
FLEXIBILITY OF USE	POOR	GOOD	FAIR	GOOD	GOOD	GOOD
RESULTS OVER WIDE AREAS	FAIR	GOOD	POOR	POOR	POOR	POOR
DETAIL WORK	POOR	FAIR	GOOD	GOOD	GOOD	GOOD
USER SAFETY	GOOD	GOOD	FAIR	POOR	FAIR	GOOD
PURCHASE EXPENSES	GOOD	POOR	GOOD	GOOD	GOOD	GOOD
RUNNING EXPENSES	GOOD	GOOD	GOOD	FAIR	FAIR	GOOD
DISADVANTAGES	TOD MUCH WATER		LEAVE SOLID SALTS	HEALTH HAZARD		DANGER OF SHOCKS

3. Comparison of cleaning methods.



The cleaning of surfaces: "nebulization chamber". With this system, mechanical action of the surfaces is reduced to the minimum.

The method most extensively used for cleaning was treatment of the surfaces with nebulized water (note 2) which permits the surface deposits, including some of the "black crust", to be solubilized while fully respecting other surface features of historic interest (protective coatings, graffiti, traces of stone working, etc.).

The equipment is composed of autonomous, adjustable nozzles (up to a max. of 24), spraying a mixture of 24 lt/min of air and 3.4 lt/h of water. It functions at about 2 bars of pressure. The plant is fed by a surge tank for the water and a continuous air compressor at 1500 lt/sec. Compared to nebulizers normally available on the market, this system utilizes little water, so that by aiming the jets properly one can avoid dripping and surface runoff.

For this operation, "nebulization chambers" are rigged up from time to time with polyethylene sheets. These enable us to work in a wind-free situation, maintaining the equipment about 2 m away from the surface with the nozzle pointed upward so that microscopic particles of water fall on the marble indirectly. With this system, mechanical action on the surfaces is reduced to the minimum, and in particular is limited to light brushing with soft brushes after each application cycle, to remove the particles solubilized by the water.

A drainage system prevents the water from passing to lower levels.

On average, each treatment covers an area of 1 m², and is applied in three cycles of 3 hours each, including pauses for operator inspection and for any necessary ongoing consolidation. After this begins the long and delicate work of removing especially tenacious deposits.

It is worthwhile to stress that what might appear to be a semi-automatic cleaning system actually requires continuous attention, with assiduous checking to be sure that the dissolution of a compact deposit does not expose areas of disintegrated marble that could be damaged even by the gentle nebulized water. When this happens, the treatment must be momentarily suspended and the marble repaired by consolidation or micro-puttying.

The cleaning is concluded with the use of rotating or percussion micro-drills, powered pneumatically (for safety reasons, electrical equipment is restricted on scaffolding where water is in use) or spot applications of compresses imbued with a neutral or slightly basic pH cleaning agent (AB57) [5] (photo 2).

Consolidation

A Roman commemorative monument such as the Arch of Septimius Severus is certainly an expression of sculptural art, but it is first of all an architectural structure with inherent structural rules and static requirements. Thus consolidation operations must deal with both aspects. In this context we tried, wherever possible, to apply a common ethic in the choice of materials and techniques, varying principally in the forms of application. Our goal was to obtain homogeneous surfaces at the end of operations, just as the original situation was homogeneous (all marble). Thus, for example, we did not want to have a divergence between the materials used to repair large structural sections (true fissures in the structures with portions of blocks missing) and for puttying areas of medium-to-small dimensions (cracks from 4-5 cm down to 1-2 mm) or even between micro-puttying (cracks smaller than 1 mm) and the surface consolidation (which replaces or supplements the preconsolidation during cleaning).

All this, naturally, had to be accomplished without carrying any method to an extreme, because some features must still be respected: some in-depth consolidations must always be carried out with acrylic resins (for their penetration capacities, for example), or else some fragments should be re-adhered with epoxy resins (for their adhesive power) and so forth.

Thus we began, first experimentally and then more extensively, to utilize lime-based techniques, developed in the Roman era and transmitted to us through archaeological evidence, historical sources and reminiscences of workshop practice and tradition.

The basic requirement was to have a supply of lime slaked according to traditional canons [6], together with a reacquisition of the craftsman's manual skill, which is no longer taught in any "modern" professional training programmes.



3. Superficial consolidation with hydraulic lime-based technique

For the lime, we used a lime slaked for about three years in old Roman slaking pits near the Domus Tiberiana; these pits were restored specifically for this purpose (note 3).

Alternatively, we used a low-salt alkaline hydraulic lime in the manner described below [7].

We will begin with the repair of large fissures (up to 50 cm wide, some metres high and 40-50 cm deep), often with portions of detached blocks held in place with iron and lead rods, which were put in during the restorations of the mid 1800s. Here we used a double technique: first a filling of "cocciopisto" (1 part slaked lime, 1.5 of pozzolana, and 1 of brick fragments), brought to 1-2 cm below the final surface level. It is important to wet the support thoroughly before the application and to assure that the mix dries slowly. A final layer follows, brought level with the original surface and applied with the "Roman stucco" technique (1 part lime and 2 of filler - the latter being composed of 1 part marble dust, 3 of river sand, 1 of sifted pozzolana).

An essential condition for the success of the operation is to work the material constantly until it dries, polishing it repeatedly with a spatula, reminiscent of the "politiones" of Vitruvius [8], to draw the moisture to the surface of the mix and foster in-depth carbonation. To fill a thickness of 1-2 cm, one uses several superimposed layers, each applied when the one below has set. This operation also calls for slow drying (simply keep the part shaded and avoid days of intense heat, above 30°C).

When the position of the zone makes it impossible to use the "Roman stucco" technique, we use hydraulic lime in the mix together with the filler previously described. In this case it is obligatory to keep the mix in a damp environment (covering it with compresses of paper pulp and water) until it has set.

Both results were found to be satisfactory without appreciable differences.

For putting smaller cracks (4.5 cm to 1-2 mm) we used a procedure similar to the one described above for covering the "cocciopisto" filling, with similar distinctions in the choice of lime, depending on the accessibility of the surface.

Descending to very fine cracks, less than 1 mm wide, one passes to micro-puttying, for which we used hydraulic lime alone as it was obviously impossible to work over the "Roman stucco".

In this case we added Primal AC33 at 5% to the water of the mix. This was chosen because we realized on the worksite that it provided greater solidity to the material -- useful for cracks that require small amounts of putty (photo 3).

As can be seen, the passage from one operation (repair of large lacunae) to another (micro-puttying, for instance) is no longer marked by changes of technique or materials, but is connected by a single approach.

Continuing in this vein, one can note how even the distinction between micro-puttying and surface consolidation can be overthrown, as often the latter operation is similar to the former, especially in the case of badly disintegrated marble such as that on the Arch of Septimius Severus.

Thus one can understand how it was also often possible to maintain the same approach, by working with the dilution of the mix and the granulometry of the filler in order to influence the penetration (naturally this was inferior to that of Paraloid or ethyl silicate but still satisfactory) and even the chromatic results (using lime, sand and pozzolana, one can range from semi-transparency to opacity and cover, if so desired, the numerous color tones on the monument's surface)[9].

This system enabled us to deal with the problem of the consolidation carried out parallel to the cleaning. The cleaning itself proved to be a useful test of the durability of the material, as consolidated areas were also exposed to cycles of nebulized water.

Conditions for satisfactory consolidation were slowness and constancy of application (continuous brushing to soak the marble until saturation) and maintaining a very damp environment (operations were carried out inside the nebulization chamber with an R.H. close to 100%).

Integration

This operation dealt exclusively with the structural elements that functioned in the disposal of rainwater; indeed, a close relationship was demonstrated (one diagram in the graphic analysis is devoted to this) between the loss of portions of the original cornices and highly advanced forms of marble decay. For cornices without too pronounced a projection we proceeded with the same technique described above for repair with "cocciopesto" and "Roman stucco", re-forming the contours to obtain a drip course but not reproducing the decorative elements.

For the larger protruding cornices spanning the facades at three levels in accordance with a precise architectural plan, we have studied another form of integration. This involves placement of travertine slabs with drip courses, supported by the residual original parts and protruding slightly farther out. The aim was to reestablish the water disposal system without significantly disturbing the aesthetic appearance of the monument. The slabs can be put in place with fibreglass pins embedded in epoxy resin, exploiting the numerous structural holes in the areas concerned.

A series of life-size wooden models of the zones requiring integration has enabled us to study the effect and we are now in a position to pass to definitive implementation (photo 4).

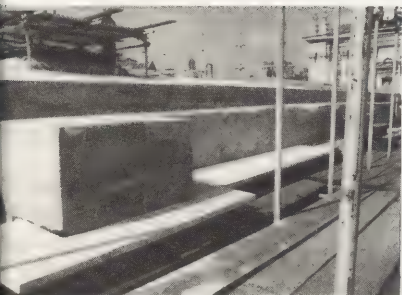
Final protection

Final protection represents, without doubt, a crucial point in the conservation of stone monuments exposed in an urban environment, and it is still a subject for research and testing. Nevertheless, some principles have been defined and thus the research is now proceeding within precise limits.

The idea of a "sacrificial surface", for example, is now an accepted concept. This would be a layer adhering to the original surface which is capable of buffering (at its own expense) the effects of environmental exchange; it is reapplied periodically and above all is capable of deteriorating without interfering with the stone surface itself (in practice it self-destructs and washes off while remaining inert).

At this point the choices focus on two distinct possibilities: one is related to the category of synthetic products, of the plastic type, and transparent (at least at the moment of application); the other pertains to the realm of semi-opaque lime-based coatings, with organic binders or mixed with modern additives.

As for this second category, we should say that the application tests carried out to date on the worksite have given very interesting results, such as to encourage us to invest further time and energy [10].



Wooden model of the integration of the upper cornice.

With regard to the condition of the surfaces of the Arch of Septimius Severus as they stand after the conservation intervention in progress, they present a homogeneous texture without any adjacent or superimposed products that are incompatible with the original material. They are ready to receive final protective treatment.

Conclusions

To conclude, some considerations are in order. The first are linked to the time required by a project such as the conservation intervention on the Arch of Septimius Severus. In particular we have seen that when an intervention in a monumental context is preceded by a long period of study and experimentation, and when a detailed working project is available, the manual implementation of the conservation interventions requires little time (apart from bureaucratic delays). Thus we have seen, after the first phases of work to confirm the planning forecasts, that 12 more months will be required to finish the southern half of the monument (now under scaffolding). Then another 18 months (still in terms of technical time) will be necessary to complete the entire intervention (including mounting and dismounting the scaffolding) and consign the monument to the workmen who should carry out the surface maintenance programme.

Indeed, it is an undoubted fact, amply demonstrated by now, that monuments do not maintain themselves unaided, and that the conservation intervention now in progress must be followed by careful maintenance routines. In this sense, in the case of the arch, every phase of the intervention (as mentioned at the beginning) is recorded on a computer with graphic capabilities -- that is to say, every part of the monument's surface has a digitalized counterpart on which is registered the state preceding the intervention, the operations carried out and the estimated duration of the materials and interventions. This ultimately means that through theoretical projections we will be able to keep up to date on the evolution of the surface situation, knowing in advance where to intervene with spot repairs, done simply from a cherry picker, and maintaining the monument above the threshold of deterioration at little cost.

One last consideration should be made to underline how in a complex and varied case such as a stone monument, involving several thousand square meters of surface area and exposed to the elements, one should always speak of preferential choices and not prejudicial ones. Any techniques or materials will offer positive aspects that can potentially be exploited under the right conditions. Thus the success of the intervention may be due to the suitable choice of one technique or another at different moments.

The Arch of Septimius Severus is above all a palimpsest in the history of Rome which, thanks to the chance, or mischance, of being neglected for so long has survived with its surfaces devastated by decay but complete in its historical stratigraphy. A rule that has become law for those of us who work in the sphere of conservation of cultural property and which is even more valid when the object is a key monument such as the Arch, is absolute respect for the original parts and surfaces, including all the transformations they contain, and also respect for all the techniques and materials that make up these parts and still sustain the original structural and aesthetic form.

NOTES

1. The intervention on the Arch of Septimius Severus is being carried out in application of the special law for Rome #92/81, and is directed by Dr. A. Melucco of the Central Restoration Institute and G. Martines, architect of the Archaeological Superintendence of Rome. The work is being done by the Centro di Conservazione Archeologica, Rome, directed by the author.
2. The nebulization plant was constructed in response to the specific requirements of the worksite concerned, with the kind permission of the Alessandri S.r.l. company. The system uses normal unsoftened water.
3. The intervention was carried out in the context of the general rehabilitation of the Domus Tiberiana under the direction of G. Martines, architect of the Archaeological Superintendence of Rome.

REFERENCES

1. M.L. Conforto et al., "Materia e storia nella metodologia di un intervento: il restauro dei monumenti marmorei romani," Manutenzione e conservazione del costruito fra tradizione e innovazione (Bressanone, 1986) pp. 726-732;
A. Melucco Vaccaro, "Studi e scoperte in relazione ai restauri dei grandi monumenti marmorei romani," Archeologia Laziale, vol. VIII (1986);
R. Nardi, "Note in margine alla frequentazione del Tempio di Vespasiano e Tito," Forma La Città Antica e il Suo Avvenire, Catalogo della Mostra (Rome: 1985) pp. 68-71.
2. G. Biscontin, et al., "Studio di stabilità di resine silconiche impiegate nella conservazione dei materiali lapidei," Manutenzione e conservazione del costruito fra tradizione e innovazione (Bressanone: 1986) pp. 597-611;
C. Conti, et al., "Il consolidamento della pietra nella dimensione del grande cantiere: metodi inorganici e organici su superfici marmoree," ibid, pp. 766-774.
3. G. Urbani, "La scienza e l'arte della conservazione dei beni culturali," Ricerche di Storia dell'Arte, pp. 7-10.
4. R. Brilliant, The Arch of Septimius Severus in the Roman Forum (Rome: 1967);
R. Nardi, "L'Arco di Settimio Severo: indagini storiche e conservative," Rendiconti della Pontificia Accademia di Archeologia, vol. LV-LVI (1984).
5. L. and P. Mora, Metodo per la rimozione di incrostazioni su pietre calcaree e dipinti murali, C.N.R., Centro di studio Cause di Deterioramento e Metodi di Conservazione delle Opere d'Arte, Rome, 1972.
6. A. Costanzi Cobau, Tecniche di pittura a secco: la pittura a calce, (Rome: I.C.R., 1984). Unpublished manuscript.
7. Ferragni, D., Malliet, J., et al, "Essais de laboratoire sur des coulis a base de ciment," Mortars, Cements and Grouts Used in the Conservation of Historic Buildings (Rome: ICCROM, 1982).
8. Vitruvius, De Architectura, Book VII, II, 2.
9. C.A. Price, K.D. Ross, "The cleaning and treatment of lime-stone by the "lime method". Part II. A technical appraisal of stone conservation techniques employed at Wells Cathedral," Monumentum (1984).
10. M. Caroe, "Wells Cathedral: conservation of figure sculptures 1975-1986. Final report and assessment," Case studies in the conservation of stone and wall painting, Bologna 21-26 September 1986, pp. 105-109.



SUMMARY

This report arises from a conservation intervention on a wall of mudbrick laid in clay, carried out in situ during the excavation campaigns for the Crypta Balbi in Rome.

This is a rare type of structure in the urban Roman context, considering its material, shape, and the construction techniques used: the reason for its rarity is, naturally, the material's own susceptibility to atmospheric agents. To carry out the intervention, we deliberately chose to use simple materials and techniques, as close as possible to the original. This was to avoid denaturing the character of the wall itself with the addition of extraneous products.

CONSOLIDATION OF A MUDBRICK WALL USING SIMPLE TECHNIQUES AND MATERIALS

Roberto Nardi
Centro di Conservazione Archeologica (C.C.A.)
Via Zanardelli 16, 00186 Rome, Italy

This report arises from a conservation intervention on a wall of mudbrick laid in clay, carried out in situ during the excavation campaigns for the Crypta Balbi in Rome.

To explain something of the background: the Crypta Balbi excavation involves an urban area in the center of Rome*, in a zone that over the past two millennia has experienced a continuous superimposition of human activity. Thus today it presents an exceptionally interesting historical stratification.

The wall is a semi-circular structure, 4.20 m in diameter and 0.80 m thick, which rises 3.70 m above the present excavation level. Without getting involved in speculation as to the dating and significance of such a structure, I might mention one hypothesis among many that it was a large kiln for materials, prepared and never used, and therefore never fired. This is a rare type of structure in the urban Roman context, considering its material, shape, and the construction techniques used: the reason for its rarity is, naturally, the material's own susceptibility to atmospheric agents.

We were given proof of the latter at the expense of the structure itself, when there were no conservators on site. The wall was a quarter excavated in plan and 1 m in elevation, and left exposed to the elements. Rain, wind, sun and algae immediately took their toll, dissolving most of the external facing, and leaving a shapeless, unrecognizable nucleus.

Due to this initial "sacrifice", the conservators were asked to extend their laboratory activity to include direct intervention on site, working alongside the archaeologists. It was thus possible to excavate the structure after first organizing some preventive measures that would limit damage and the need for later restoration.

Preventive measures

The causes of deterioration were identified as follows: rain, wind, plants and algae, sun. The rain, beating and running on the structure, dissolved the unfired clay; the wind exercised mechanical pressure and abrasion, which were particularly damaging to surfaces already weakened by rainwater; the plants and algae caused chemico-physical damage due to their growth and metabolism products; the sun heated and dehydrated the damp structure, causing the material to contract, crack and break away, as well as crystallization of soluble salts.

We therefore decided to intervene with arrangements that would permit the regular excavation process to continue without threatening the integrity of the remaining structure. A rigid roof of metal tubing and corrugated plastic was erected to keep off rainwater and limit the effect of the wind, which, thanks to adjacent structures, came primarily from above. Algae were controlled by spraying a biocide Lito 3 (Ciba-Geigy) before the spring campaign. As to the plants, a distinction was made between those growing superficially on the wall, which were cut at the roots and removed, and those growing partially within the clay structure. For these, we decided to cut off the accessible parts and leave the rest in place -- first because total removal would have caused serious damage; second, because the plants play, nonetheless, a useful role as static reinforcement.

The problem of the clay's dehydration from insolation required specific measures, because the overall schedule of the dig called for the structure to be excavated during the summer.

As we know, structures and artifacts, once buried, tend to reach a thermo-hygrometric equilibrium in relation to the surrounding environment. This, after an initial "expense" in terms of deterioration, corresponds to a stable phase during which the material does not deteriorate any further. Then along comes the archaeologist, who by excavating, alters the material's hard-won equilibrium and sets off a new, dramatic phase of "acclimatization" to the new environmental values, as the material seeks to reach a new stable phase. At this point the equation is simple: the slower the new acclimatization phase, the lesser the damage to the structure.(2)

In our case, uncontrolled dehydration would have led to the contraction of the material, with the formation of micro/macroscale cracks, spalling and surface loss; breakage and structural damage that might compromise the wall's static performance; surface migration and crystallization of dissolved salts; interference with in-depth consolidation with hydraulic grouts.

The first simple solution was to shade the structure all day with bamboo screening fastened over the corrugated plastic roof. Then we devised a humidifying system that delivered water "drop-by-drop" and was fed from a water tank that refilled itself automatically, without any use of electric power (sold for gardening and modified to obtain a minimum but continuous dosage).

This kept the structure damp for the total time necessary for excavation (even when the yard was closed for holidays) and conservation. Tests on samples made it possible to set the water dosage so that the quantity emitted was entirely absorbed deep into the structure without any puddling or overflow (1 lt/ divided into 72 outlets along the entire circumference).

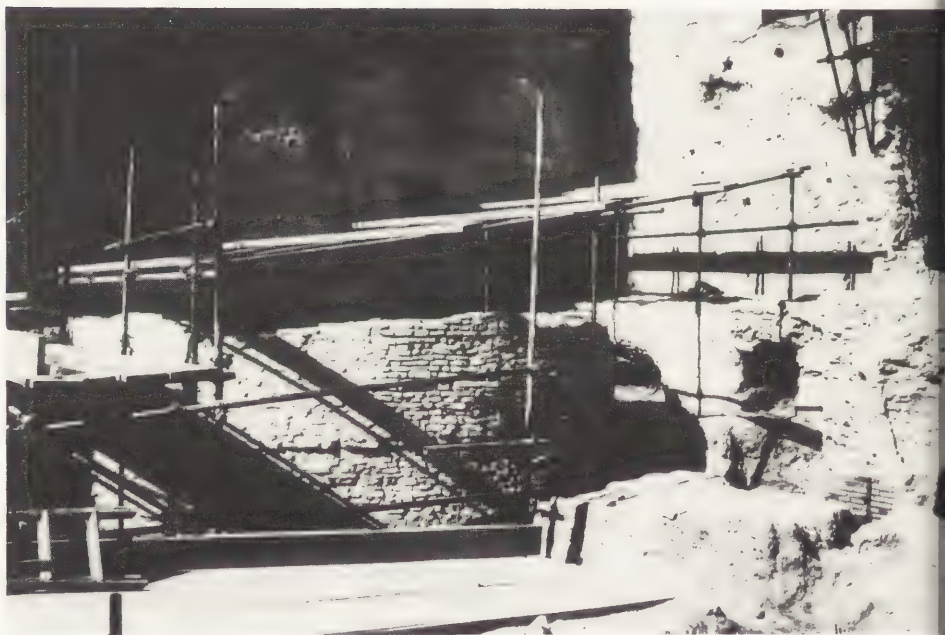


Figure 1. Wall of mudbrick laid in clay. General view showing the temporary shelter of metal tubing, corrugated plastic and bamboo screening. This roof serves to keep off rainwater and to limit insolation, overheating and drying of the clay. The wall is about 4 m high.

The intervention

To carry out the intervention, we deliberately chose to use simple materials and techniques, as close as possible to the original. This was to avoid denaturing the character of the wall itself with the addition of extraneous products. We were perfectly aware that this decision could mean less "solidity" of the wall once it was restored, but we preferred to deal with this problem by planning for future roofing and protection (and thus take a risk) rather than immediately sacrificing the appearance and the "precarious" but "genuine" character of this kind of structure, perhaps by flooding it with synthetic materials. For this we decided, insofar as possible, to use the same material of which the wall is made - clay - with a minimal addition of hydraulic lime (10% Lafarge hydraulic lime, low salt content)⁽³⁾.



Figure 2. Detail of the wall exposed to environmental agents.

A brief inquiry among some former brick makers, who had gone out of business more than 25 years ago, enabled us to locate a clay pit in the city that contained material similar to the clay in the wall (consistency, color, purity); thus we had the necessary access to raw material for the intervention.

The intervention was divided into two parts: one involved internal consolidation of the structure, with repair of cracks and reinsertion of detached blocks; the other involved integration of zones of external facing to meet static requirements, and surface protection.

The humidification plant was progressively de-activated during the in-depth consolidation; the flow of water was reduced each day until the tank was finally shut off and the plant dismantled.

For the internal consolidation we carried out infiltrations of a solution of 9 parts sifted clay, 1 part hydraulic lime, and water as needed. (The solution was considered suitable after sampling for fluidity, color and resistance. The resistance could not be excessive in relation to the original material or it would have meant inserting a rigid element into a fragile structure and upsetting the static equilibrium.) The mixture was then injected into the cracks and detached areas, which were first treated with water and alcohol. For this operation we used plastic syringes, replacing the needles (which were too fine) with either rigid metal tubes (internal diameter 3 mm) or flexible polyurethane ones (Festo Pneumatic PU3, internal diameter 3 mm), varying in length from 10-50 cm. Different injection tubes were used in accordance with the internal formation of the cracks being filled and the depth of the consolidation. Holes to inspect and/or facilitate the filling of the cavities were occasionally drilled with a hand drill, using bits 2-3 mm in diameter.

Where necessary the larger detached zones were re-positioned against the body of the structure by means of expanding braces, which were removed once the mixture dried. As an indication, the consolidation of about 19 m³ of wall required 60 kg of grout, equal to 3 kg/m³.

The consolidation terminated with microstuccoing and stuccoing of all surface cracks. This was done with a spatula and the same clay-lime mix as before, prepared in denser form.

For the second type of intervention (repair for static purposes where the external mudbrick facing had fallen away) we adopted the compromise of inserting "half-baked" bricks. For this, another sampling was done, this time with a potter's kiln. Progressive tests of firing were made in increments of 100°C (from 100° to 900°C) on clay samples with different amounts of sand added to the mix, in order to study their behavior on cooling, color changes, and resistance.

The samples thus obtained were subsequently tested for resistance to artificial rain. The desired result was to obtain bricks that were as similar as possible to the original mudbrick (in size, shape and color) but resistant to water, and to use graphic documentation in order to avoid the risk of falsification.

This was in order to make statically solid integrations (as they had to serve as supporting ribs on the sides of the structure) which would also eventually act as an impermeable outer protective barrier.

Unfortunately, the results were not exactly what we had hoped, due to the relatively high firing temperature required to make the clay impermeable (above 400°C), which produced a color distinctly different from that of the mudbrick. At least the areas of integration will now be easy to distinguish from the original structure.

For surface protection we also decided to use a "light" approach that would permit consolidation of surface areas with a "dusting", which was not expected to act as a water repellent. We therefore used a very liquid solution of lime milk and sifted clay, sprayed on.

This solution, as mentioned above, functions solely as a surface consolidation and a sacrificial layer, being a front for contact with the environment and a new location for crystallization of soluble salts; the question of protection from rainwater was ultimately to be resolved by roofing.

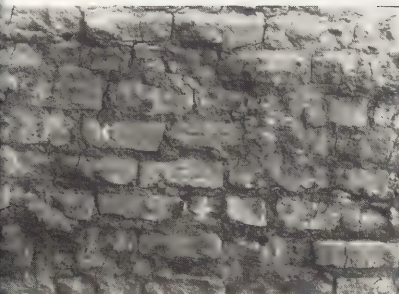


Figure 3. Detail of the wall excavated during the conservation intervention. The structure has maintained its original texture and consistency.



Figure 4. The "drop-by-drop" wetting system enabled the archaeologists to deepen the trench prior to a consolidation intervention, and kept the wall from drying out and running the risk of contraction, crack formation or total collapse.



Figure 5. Consolidation with infiltrations of a clay solution combined with 10% hydraulic lime.

Finally, we decided not to attempt to extract the soluble salts. In the first place, the wall is built on ground that could potentially furnish an inexhaustible supply of new salts. Thus our efforts would serve only to stimulate the circulation of dissolved salts up to the surface, creating a risk of damage to no avail. Second, after the intervention and the drying of the structure, and after 24 monthly inspections, the phenomenon of crystallization has not appeared in any significant way.

Conclusion

As we have seen, the intervention was carried out with simple preventive measures and with generic materials, relying on operations that are closer to normal maintenance practice than to extraordinary restoration. Twenty-four months have passed since the structure was excavated and it is still in a good state of conservation. Naturally, this is not a very long time, and the structure still requires inspection and occasional attention, but the result is still significant in view of the vulnerability of a material such as mudbrick in a climate such as Rome's.

This work has been presented in order to emphasize how a "light" approach in conservation can produce "heavy" results, without the use of tons of synthetic products. We deliberately chose to move away from the now almost "traditional" type of conservation intervention that calls for massive use of synthetic products, applied to incompatible substrates. This approach signals the mutation of our profession as "conservators" (of form and materials) into that of "transformers" (of original artifacts into "healthy objects").

While attributing to research laboratories the fundamental role of support in borderline cases for which light interventions would be inadequate, we also wanted to re-claim for "field" conservation a role of research in the context of the material feasibility of interventions that use simple techniques and products, compatible with the original materials and technology.

This line of work, apart from its obvious theoretical value, has important practical implications. The "official world of conservation", composed of the few countries and institutions that benefit from advanced technology and that are viewed as models, are rapidly outdistancing the others, thus dramatically increasing the gap between this elite and the rest of those responsible for cultural property. The price is paid, not only by the heritage itself, but also by the "followers" who suffer in the form of professional frustration for not being "technologists", and who often, as a result, give up trying to work with the means at hand and, worse still, abandon the traditional manuals of care and maintenance that are themselves part of the world cultural heritage.

* This corresponds to the city block formed by Via Caetani, Via delle Botteghe Oscure, Via dei Polacchi, and Via dei Delfini. The work began in November 1981, and is directed by M.L. Conforto of the Archaeological Superintendency of Rome and by Prof. D. Manacorda of the University of Siena. To date, a variable number of archaeologists -- researchers, graduates, students -- from various Italian universities have participated in the excavation, up to a maximum of 70 per campaign. There have been six campaigns interspersed with laboratory research activities. The results of the work are published contemporaneously with the excavation: three volumes are already available, and three others are in preparation. The intervention was carried out by M. Anastasi, A. Costanzi Cobau, L. Demitry, R. Nardi, C. Tavazzi, M. Van Molle, of the Centro di Conservazione Archeologica (C.C.A.), Rome.

References

- 1) D. Manacorda, Archeologia Urbana a Roma: il Progetto della Crypta Balbi (Florence: 1982).
Un "Mondezzero" del XVIII Secolo. Lo Scavo dell'ambiente 63 del Conservatorio di S. Caterina della Rosa (Florence, 1984).
Il Giardino del Conservatorio di S. Caterina della Rosa (Florence, 1985).
- 2) G. de Guichen, "Object Interred, Object Disinterred", Conservation on Archaeological Excavations. (Rome: ICCROM, 1983)
- 3) D. Ferragni, J. Malliet, et al, "Essais de laboratoire sur des coulis a base de ciment," Mortars, cements and grouts used in the conservation of historic buildings (Rome: ICCROM, 1982).



SUMMARY

The color change of stone by impregnation with silane was experimentally studied in the laboratory by using colorimeter. The following results were obtained by the experiment:

) The more amount of silane was impregnated, greater the difference of color the stone exhibited.

) The difference of color was dependant mainly on the fall in value and negligibly on the difference of chroma and hue.

) After an artificially accelerated deterioration treatment, all the stone samples showed almost the same color, which was nearly the same as their original color, while the hydrophobic effect of the stone samples given by the silane was still found adequately.

This study confirms the experientially noticed fact that stone is darkened by impregnation with silane, but regains its original color with time in outdoor conditions while it keeps the effect of treatment with silane.

LABORATORY TEST ON THE COLOR CHANGE OF STONE BY IMPREGNATION WITH SILANE

Tadateru Nishiura

Senior Conservation Scientist

Tokyo National Research Institute of Cultural Properties

Department of Restoration Techniques

13-27 Ueno Park, Taito-ku, Tokyo, 110 Japan

Introduction

Impregnation with silane is very effective in consolidating and/or hydrofugating stone for its conservation. But one of the problems of impregnation treatment of stone with silane is that it sometimes changes the color of the treated stone significantly. The mechanism of the color change of stone by treatment with silane, which is a transparent liquid when applied and hardens to a transparent glassy gel, has not yet been clearly elucidated, though it is often explained as a change in index of refraction. The elucidation of the mechanism should be basic in solving this problem of color change. Thus as a first step, the characteristic of the color change was experimentally studied in the laboratory by using color meter.

Experimental

1. Test Materials

1.1 Stone

Grayish porous tuff, which is said to suffer quite often from serious color change by impregnation with silane, was employed as stone sample, since this type of stone is widely used for stone monuments in Japan. The bulk density, the real density and the porosity of this stone are 1.50 g/cm³, 2.69 g/cm³, and 44.3 % respectively. 4 stone pieces (5×5×5cm) were cut out from each of the 3 stone blocks (A, B, C) as test pieces.

1.2 Silane

A solution of the oligomer of methyltriethoxy silane in organic solvent (Trade name, SS-101) was used for the test. This hydrophobic silane solution has been widely applied as consolidant and/or water repellent for the conservation of stone in Japan. The silane cures within 24 hours at room temperature by adding a catalyst (tin compound) 3-5 %.

1.3 Colorimeter

Colorimeter used in this test was Color Computer SM-3-SCH (Suga Test Instruments Co., Ltd). Color factors X, Y and Z were measured by the color meter. Then, according to the CIE 1976 (L*, a*, b*) formula, the difference of color (ΔE*ab), and then the difference of value (ΔL*), of chroma (ΔC*) and of hue (ΔH*) were calculated as follows:

$$L^* = 116 (Y/Y_0)^{1/3} - 16$$

$$a^* = 500 [(X/X_0)^{1/3} - (Y/Y_0)^{1/3}]$$

$$b^* = 200 [(Y/Y_0)^{1/3} - (Z/Z_0)^{1/3}]$$

$$C^* = (a^{*2} + b^{*2})^{1/2}$$

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

$$\Delta L^* = L_2^* - L_1^*$$

$$\Delta C^* = C_2^* - C_1^*$$

$$\Delta H^* = [(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2}$$

$$X_0 = 98.05, Y_0 = 100.00, Z_0 = 118.10$$

2. Test Method

On one face of each of the 12 stone test pieces (3 sets of 4 pieces each), an identification number was marked. The color of a circular area with a diameter of 30 mm on all of the five remaining faces, was measured for each piece, and the mean of the five measurements was made the color of that piece.

Then the stone test pieces were dried in a 60°C oven for 2 hours. After being cooled down to room temperature in a desiccator containing silica gel, No. 2, 3 and 4 of each set were impregnated with the silane solution SS-101 by immersing them in it for a certain time. The content and the impregnation depth of the silane solution in the stone pieces are shown in Table 1. The impregnation depth was measured by observing the hydrophobicity on the inner face of the stone pieces after cutting it from the center (Fig. 1). So, needless to say, this measurement was done after all the tests.

After the impregnation treatment, the stone pieces were kept at room temperature for 7 days, followed by drying in a 50°C oven for

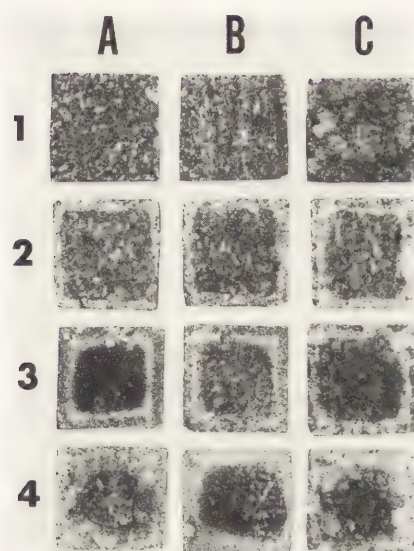


Fig. 1 Measurement of depth of silane impregnated layer (light colored margin)

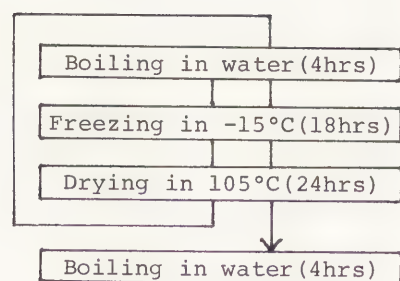


Fig. 2 Artificially accelerated deterioration treatment

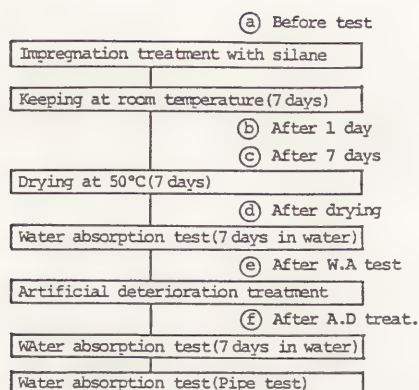


Fig. 3 Diagram of the experiment procedure

Table 1 Treatment of stone sample with silane solution and content of the solution by the treatment

No.	Impregnation treatment	Content of silane solution (wt%)	Content of silane solution (kg/m ²)	Impregnation depth (cm)
1	Control	0	0	0
2	Impregnation (5 mins.)	8.4~9.8	1.19~1.27	0.5~0.8
3	Impregnation (15 mins.)	12.3~12.9	1.61~1.74	0.8~1.0
4	Impregnation (60 mins.)	16.8~17.5	2.24~2.33	1.0~1.5

another 7 days. During this time, their color was measured after the 1st day and after the 7th day of keeping at room temperature and after the 7th day of drying at 50°C.

The stone pieces were then immersed in water for 7 days to measure the rate of water absorption in them. Then after drying them at room temperature until they got their constant weights, their color was measured.

Next they were subjected to an artificially accelerated deterioration treatment as shown in Fig. 2. Then, after drying them at room temperature to constant weights, their color was measured.

After drying them at 50°C to constant weights, they were immersed in water for 7 days to measure the rate of water absorption in them again.

Finally, after drying them at 50°C to constant weights, their water absorbability was measured by pipe test.

The procedure mentioned above is diagrammatized in Fig. 3.

3. Test Results

3.1 Color Measurement

The difference of color ($dE = \Delta E^*ab$) of the stone test pieces at each step from their original color (dE on (b)-(f) from (a) in Fig. 3) are shown in Fig. 4. Fig. 4 clearly shows that the longer the stone was treated, namely the greater the amount of silane impregnated, the greater the difference of color (dE) the stone exhibited, and that the dE decreased by the artificially accelerated deterioration treatment so that all the test pieces showed almost the same color, which was nearly the same as their original color. Small increase in dE of all the test pieces after the water absorption test (after 7 days' immersion in water) is considered to be due to the fact that the piece were slightly colored by the water in which the red ink used for numbering dissolved a little bit.

In Fig. 5, the difference of color (dE) is analyzed into three elements of color: the difference of value ($dL = \Delta L^*$), the difference of chroma ($dC = \Delta C^*$) and the difference of hue ($dH = \Delta H^*$). In this case, the amount of the difference of the three elements of the control (No. 1) is subtracted from the ones of the treated pieces (No. 2, 3 and 4) and it is shown by a dotted line because this amount is considered comparable to the above mentioned coloring by the red ink. Fig. 5 clearly shows that the difference of color (dE) is dependant mainly on the fall in value and negligibly on the difference of chroma and hue, which is more plain when the dE is the greater. Hereby, the color change of the stone by impregnation with silane proved to be a darkening of color.

3.2 Water Absorption Test

The rate of water absorption in the stone sample B before and after the artificially accelerated deterioration treatment is shown in Fig. 6 (Sample A and C gave almost the same result as B). Fig. 6 clearly shows that water absorbability in the stone was greatly decreased by the impregnation treatment with silane, and that the hydrophobicity is more or less diminished by the artificially accelerated deterioration treatment.

In order to quantify the hydrophobicity and its diminution by the deterioration treatment, Anti-Water-Absorption Coefficient (A.W.A.C) after 1 hour, 4 hours, 1 day and 7 days of immersion in water of the sample B are shown in Table 2.

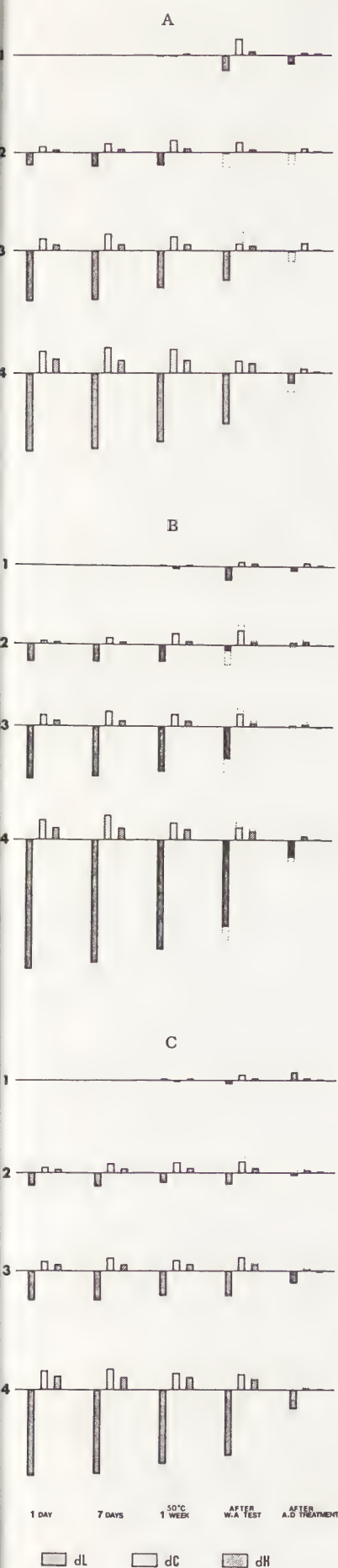


Fig. 5 Difference of value, chroma and hue at each step of the test

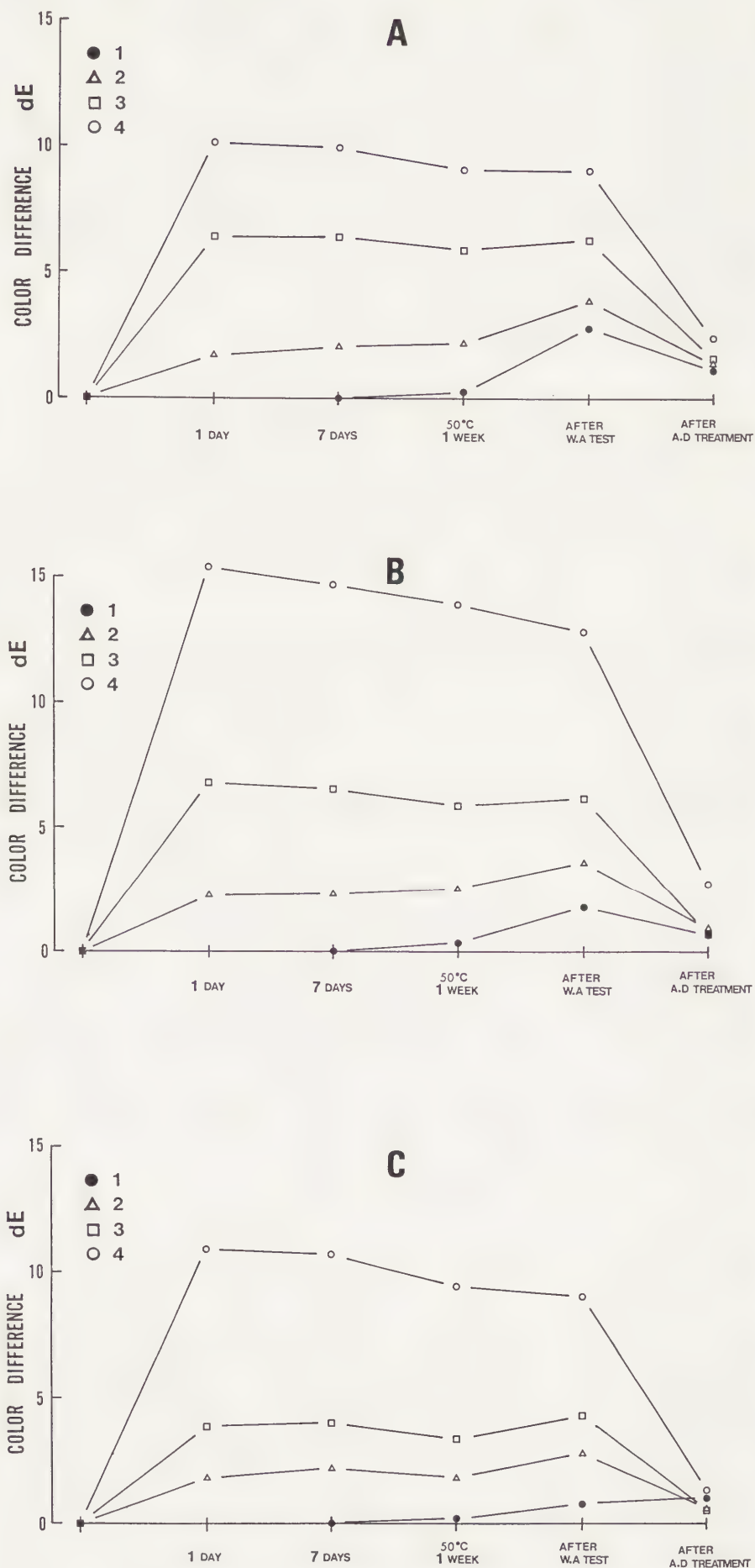


Fig. 4 Color difference at each step of the test

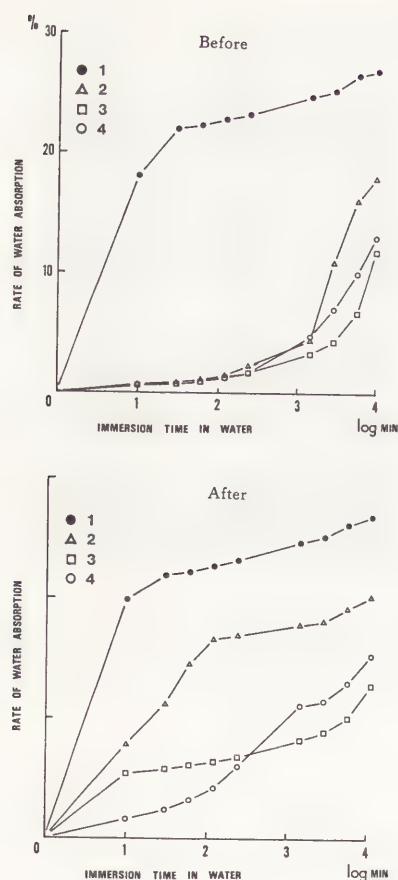


Fig. 6 Water absorption by immersing in water (sample B)

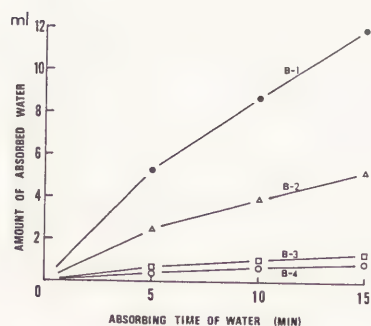


Fig. 7 Water absorption by pipe test of sample B after artificially accelerated deterioration treatment

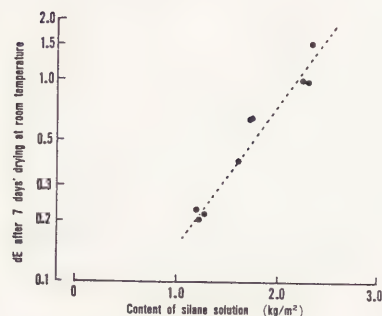


Fig. 8 Relationship between silane content and color difference of stone sample

Table 2 Anti-Water-Absorption Coefficient before and after artificially accelerated deterioration treatment

Sample	Immersion time in water											
	1 hr.			4 hrs.			1 day			7 days		
	(1) Before	(2) After	(2)/(1)	(1) Before	(2) After	(2)/(1)	(1) Before	(2) After	(2)/(1)	(1) Before	(2) After	(2)/(1)
B-1	0	0	—	0	0	—	0	0	—	0	0	—
B-2	9.5	3.5	0.37	9.0	2.7	0.30	8.2	2.8	0.34	3.3	2.5	0.76
B-3	9.6	7.3	0.76	9.3	7.1	0.76	8.7	6.7	0.77	5.6	5.2	0.93
B-4	9.6	8.6	0.90	9.3	7.4	0.80	8.1	5.5	0.68	5.2	4.3	0.87

Here, A.W.A.C. = $(R - R') / R \times 100$

R : Rate of water absorption in control stone

R' : Rate of water absorption in silane treated stone

Table 2 shows that, B-3 and 4 retained 70 to 80% of their hydrophobicity after the artificially accelerated deterioration treatment, while B-2 kept only 1/3 of it.

Immersion of stone in water may be a too severe way to evaluate its water absorbability. Thus, in order to estimate absorbability of rain water in stone, pipe test is considered more practical. Fig. 7 shows the result of the pipe test for sample B after the artificially accelerated deterioration treatment. It is clear that B-3 and 4 retained very high hydrophobicity even after the deterioration treatment.

DISCUSSION

The experiment gave the following results:

- 1) The color change of the stone sample by the impregnation with silane was proportionate to the amount of the impregnated silane. The relationship between the degree of the color change [dE] of the stone sample and the amount of the impregnated silane [R(kg/m²)] was, in this case, $\log dE = kR + C$ (K & C are constant) as shown in Fig. 8.
- 2) The color change was mainly a fall in value, and the difference of chroma and of hue were negligibly small.
- 3) By the artificially accelerated deterioration treatment, the color change was greatly diminished so that all the pieces showed almost the same color, which was nearly the same as their original color, while they still retained adequately their hydrophobicity given by the silane treatment.

It can be said that the above results confirm the following fact which is experientially noticed among conservators, restorers and others:

The color change of stone by impregnation treatment with silane is a darkening of color which increases in proportion to the amount of impregnated silane. This darkening gradually decreases with time in outdoor conditions and finally becomes unnoticeable, while the stone keeps the effect of the treatment with silane if it has been impregnated sufficiently.

ACKNOWLEDGEMENT

The author is greatly indebted to Mr. Seiji Higuchi, Tokyo National Research Institute of Cultural Properties, for his very valuable advice. And he is also deeply grateful to Mr. Hiromichi Murakami, Japan Association for Conservation of Architectural Monuments, for his kind help in preparing the stone sample.

SUMMARY

The causes of decay of a Sydney sandstone building, St. Mary's Church, Balmain, are discussed as an example of the type of decay processes affecting stone buildings, monuments and statuary within the Sydney region.

Background information on the commissioning of the Conservation Report and Maintenance Programme is given, with discussion of the building's cultural significance.

The petrography of two types of Sydney sandstone is described together with a description of the local environmental conditions to which stone is exposed.

The uncontrolled entry of water and its contaminants is identified as the common cause in each of the main decay processes active at the church.

The author's conference presentation will follow up this paper with discussion and description of the techniques being used for the building's repair and protection.

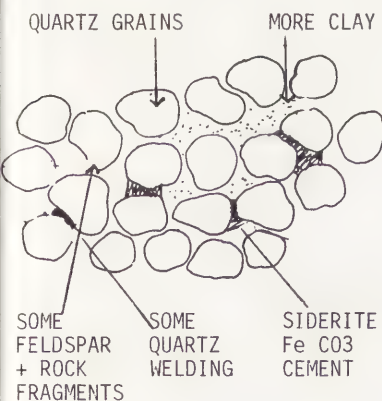


FIG.1. ILLUSTRATION OF MATRIX OF "YELLOW BLOCK" SANDSTONE

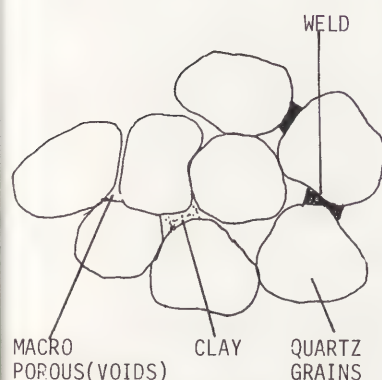


FIG.2. ILLUSTRATION OF MATRIX OF "WHITE" SANDSTONE

THE CONSERVATION OF ST. MARY'S CHURCH BALMAIN, SYDNEY - THE APPROACH AND ANALYSIS

ROSS TAYLOR
DIRECTOR (CONSERVATION ENGINEER)
T.A.TAYLOR & SON PTY.LTD.,
40 Robert Street,
ROZELLE SYDNEY AUSTRALIA

1. INTRODUCTION

Sitting up on a hill in suburban Sydney is a very plain, frail, somewhat bedraggled old church. If it were just like any other street derelict it would attract little attention or concern- however this church has hidden treasures. The existing main fabric of "white" Sydney Sandstone was built in 1859 as an extension to an original small chapel. The chapel was built in 1848 by the famous Architect Edmund Blacket, out of "Yellow Block" Sandstone. Blacket was one of Australia's early Architects and the original chapel is one of his first uses of the perpendicular gothic style which occurred later in many of his projects. The cultural significance of this chapel is unquestioned as there are precious few of his buildings remaining intact.

In addition there is evidence that Blacket provided some of the handiwork for enrichments such as stained glass panels to the chancel. The front section of White Sandstone is less significant, being designed by the firm of Weaver and Kemp. It has however stood for over half the life of European settlement in Australia and it represents one of the last remaining examples of the use of "White" Sandstone in the Sydney Region.

Due to the overall high level of cultural significance of the church a Conservation Report and Maintenance Programme has been commissioned by church authorities with support from the N.S.W. Heritage Council.

It is intended for the process of Conservation to be considered in 4 main phases:-

1. Analysis and Emergency Repair
2. Repair
3. Protection
4. Maintenance

At the time of submission of this paper the Analysis and emergency repair phase are underway. This paper is essentially background briefing to the project and discussion of the stone decay processes which are evident at St. Mary's - processes which are typical (to varying degrees) to stone buildings, monuments and statuary throughout the Sydney region. Discussion is restricted to the stone elements of both the 1856 and 1859 sections.

2. DESCRIPTION AND CURRENT CONDITION

The original 1848 section is of Sydney sandstone with the popular name of "Yellow Block". The stone is of fine to medium grain. There is both quartz welding and clay bonding of quartz particles resulting in a compact stone of low porosity - Yellow Block was used extensively in the second half of the 19th century for construction of major public buildings. While the roof to this section has suffered structural failure causing an outward lean of the walls, the stone is in excellent condition with little evidence of decay.

The 1859 section is of Sydney "White" Sandstone, an essentially siliceous stone with extensive quartz/silica cementing between quartz grains. Fig.2. It is a macro porous stone with a small proportion of siderite present as a "cement". Its condition is extremely poor with extensive fretting, crumbling and cracking to most of the facade but predominantly at high level. Poor masonry construction technique combined with inadequate roof framing has resulted in substantial lateral thrust to walls and buttresses.

Considerable cracking (up to 25mm wide) and dislocation of stonework has occurred at all wall junctions and buttresses. A detailed structural report is being prepared by the Sydney Engineering Firm of McBean & Crisp. Fig.3.

The cracking and decay has proceeded to the point where safety of users is at risk. Pieces of stone of up to 300mm in size have recently fallen near congregation areas. The rate of decay is such that the 1859 section will be rendered unusable within 5 to 10 years without intervention, jeopardising access to the original Blacket section of work.

3. ANALYSIS

The extreme decay in the "White" Sandstone compared with the Yellow Block can be attributed to its poor resistance to the essentially chemical and physico-chemical decay processes operating in the Sydney region. While these processes are common to most Northern Hemisphere industrialised cities, there are some aspects peculiar to the Sydney region.

3.1. CHEMICAL DECAY PROCESSES

A recent study of the acidity of summer rainfall in Sydney revealed a mean

THE CONSERVATION OF ST. MARY'S CHURCH BALMAIN, SYDNEY - THE APPROACH AND ANALYSIS



FIG.3. CRACKING AT WALL
JUNCTIONS DUE LATERAL
DISPLACEMENT OF ROOF LOADS

pH of 4.44, the lowest reading being recorded at 3.6., Nitric and sulphuric acids being the main contributors. The main source of sulphuric acid in the Sydney region has been the combination of fossil fuels which release SO_2 into the atmosphere. The macro porous structure of the "White" Sandstone has allowed relatively free entry of acidic rain to penetrate its mineral surface where the acids' small H^+ ions breakdown the silica welding of quartz grains. This "leaching" process then allows the lightly packed clay component in the matrix to be worked out.

By comparison the compact, less porous "Yellow Block" stone is less dependent on silica welding of quartz grains and therefore virtually unaffected by leaching.

3.2. PHYSICO-CHEMICAL DECAY PROCESSES

The church is sited adjacent to Sydney Harbour and about 15km from the Ocean. It is therefore highly exposed to salt-laden wind and rain. The annual input to the Sydney area of soluble atmospheric components is $70\text{--}90\text{t/km}^2$ - the majority of these being sea-salts.

The deposition and absorption of salts of marine origin by the facade is a major source of decay. The macro-porous white sandstone freely admits salt-laden moisture with the fractures and open joints increasing the effective area of exposed stone.

Sub surface crystallization of the saline solution then breaks down the silica/quartz welds in the classic manner.

The formation of crystalline gypsum within the stone also contributes to fretting but to a much lesser extent. The presence of calcium sulphate, formed by the reaction of sulphuric acid-laden rain with calcite, within the stone matrix, has greater significance as a contributor to the formation of case hardening in "Yellow Block" stone. There is minor incidence of exfoliation of case hardened layers in the "Yellow Block" stone of the 1848 section at parapet level and to tracery of a stained glass window.

3.3. PHYSICAL DECAY MECHANISMS

Sydney's weather patterns produce short sharp changes in temperature. Diurnal surface temperature changes of 60°C are common - recently a 30° increase in half an hour. Similarly rainfall tends to be intense and of short duration. A recent rainstorm produced 235mm of precipitation in 3 hours with 412mm recorded over the corresponding 48 hours. When these extremes of temperature and moisture coincide, internal stone can be expanding while external layers are contracting thereby building up stresses within the matrix.

While this process is not a factor in the fretting and crumbling of stone at St. Mary's, it does contribute to exfoliation of case hardened layering in "Yellow Block" and exacerbates fracturing within the "White" Sandstone material.

The most significant physical decay mechanism is the corrosion of mild steel ties which were used extensively to locate enrichments and tie adjoining blocks. Volume increases, in corroded steel ties, of up to 400% have been observed at St. Mary's. If left unchecked these metallic inserts have the potential to expand by 1000%. Fracturing as a result of these volume changes has already caused the loss of 300mm section of stone from the 1859 facade parapets with many smaller pieces ready to fall.

CONCLUSION

While more detailed petrographical analysis may assist in quantifying the contribution of each process to the decay of the church stone, it can be concluded that the common factor and essential cause of decay is the uncontrolled entry of water and associated water-borne contaminants.

A repair specification will be developed with the essential purpose of tying back loose stone and modifying the movement of water into and over the stone surface.

It is anticipated that the repair and protection works will be underway before the commencement of the conference. The presentation for the conference will therefore concentrate on discussion and illustration of these repair and protection techniques.

THE CONSERVATION OF ST.MARY'S CHURCH BALMAIN, SYDNEY-THE APPROACH AND ANALYSIS

In determining these techniques and preparing a long term maintenance programme a number of choices will need to be made between technical options. If the building is to be properly conserved these need to be made with due regard for the principles of conservation and with respect for the limitations of the clients financial resources. In this way the conservation process can be seen to be the synthesis of conservation ideals with the practical limitations and opportunities of technique and finance.

BIBLIOGRAPHY

Taylor, R.J. "The Decay of Sydney Sandstone:
Its Causes and Control".
Undergraduate thesis, N.S.W.
Institute of Technology, 1983.



FIG.4. ST.MARY'S CHURCH, BALMAIN, SYDNEY - 1859 FACADE



FIG.5. DETAIL OF DECAY TO "WHITE" SANDSTONE ENRICHMENTS



SUMMARY

In connection with the restoration of the 15th century white stone (lime-stone) sculpture of St. George the Dragon-slayer, created by Basily Yermolin, there were conducted physico-chemical investigations of certain fragments of the sculpture whose aim was to determine the authenticity of these fragments.

CERTAIN INVESTIGATIONS OF FRAGMENTS OF THE ST. GEORGE SCULPTURE FROM THE KREMLIN MUSEUMS, MOSCOW, WITH A VIEW TO ASCERTAINING THEIR AUTHENTICITY

O.V.Yakhont, V.N.Yarosh, M.I.Filimonova
All-Union Research Institute of Restoration (VNIIR)
Krestyanskaya pl., 10
Moscow 109172
USSR

Stone fragments of a sculpture, which had partially retained polychrome painting, were sent in from the Moscow Kremlin museums in 1981. It was known from museum documents and the testimony by old workers that these stones were later restoration fragments of the famous sculpture of St. George the Dragon-slayer, carved and installed on the Frol-and-Lavr Tower of the Moscow Kremlin in 1464 by the architect and sculptor Vasily Yermolin. The sculpture of St. George the Dragon-slayer is the only one in old Russian art having a precise date of creation and authorship. This was established from a copy the so-called "Yermolin Chronicle".

It was dismantled in 1929 when a necessity arose to move the sculpture to new premises. About the same time the curator of the sculpture, who carried authority with specialists, made an unconditional statement (laid down in the museum inventories) that the 15th century original was the limestone bust of St. George alone, all the rest, the lower part of the figure, horse and dragon, was made of concrete and, therefore, recently.

It became further known that that the bust of St. George was transferred to the State Tretyakovskaya Gallery in 1940. In April, 1945, the Scientific Council of the Monuments Protection Department, headed by the academician I.E.Grabar, and which conducted an examination of the architectural monuments of the Moscow Kremlin, including the fragments of the St. George sculpture remaining in the Kremlin, decided upon joining the odd fragments and carrying out the restoration of the sculpture. But this decision was practically impossible to implement in the post-war period of the rehabilitation of the country's economy.

During a repeated examination of these fragments in the late 1970s experts from restoration institutions expressed doubt as to the correctness of the 1929 conclusion that the lower fragments of the St. George sculpture were made of concrete. It was right then decided to send these fragments to the USSR Scientific Research Institute of Restoration (VNIIR) for investigations and, if they are original, to carry out their conservation and restoration.

The task of these investigations was to determine the authenticity of the remaining lower fragments of the sculpture. For this purpose, a physico-chemical investigation was conducted, which showed the identity of fragments in their composition and origin.

The reason for the 1929 error, made by museum workers, can be explained by the fact that many lower fragments have a concrete and gypsum coating. These coatings appeared on the sculpture at a later time - during its restoration. Thus, twenty-seven years after its installation on the tower (in 1491) the old tower was pulled down and another tower, remaining at present and later named the Spasskaya Tower of the Moscow Kremlin, was built in its stead. The sculpture was first moved to a structure, specially built to house it, and afterwards, to the Voznessenski Monastery there in the Kremlin. The sculpture was moved from one place to another more than once, and it is not always known when. Besides that, the Kremlin and all the monuments in it were several times destroyed (in 1571, 1612 and 1812), which had an indisputable effect on the sculpture. Since this image of St. George the Dragon-slayer was very much revered and was also coat of arms of Moscow, it was every time restored. When restoring monuments of the Moscow Kremlin after Napoleon's invasion in the 19th century the sculpture fragments were coated many times with cement which was used as binding and completing material.

Later coatings, overpaintings and completions began to be intensively removed in the 1920s, by analogy with ancient monuments, from many monuments of old Russian art with the aim of a scientific investigation and restoration. The task and evaluation of these works in that period depended traditionally not upon a

technical and technological analysis (which only just began to be introduced into restoration), but upon the style and character of the revealed painting or sculpture.

The introduction of modern investigation techniques into restoration was able to facilitate an arrival at only one solution of the problem set. To do so, we employed the following techniques: petrographic, X-ray phase and micropaleontological analyses.

The X-ray phase analysis technique made possible a precise determination of the nature of the stone of the principal part - St. George's figure - and an isolation from among a large number of fragments those most close to it in composition (see the Table). The Table contains the results of the X-ray phase analysis, made on the URS instrument. The samples of stone under investigation were coated, in the form of suspension, on quartz cuvettes. The photographing was done under the following conditions: voltage 35 kV, current 12 mA, irradiation λ Cu α .

As can be seen from the Table, the material of most fragments of the sculpture is nearly pure calcite, the values of whose lattice spacing coincide fully with the ASTM data (the Table, p. 1, columns 4-6).

It is noteworthy that the material of the undamaged upper part of the sculpture is also calcite (the Table, p. 6). Thus, the X-ray phase analysis demonstrated that the material of St. George's figure and most fragments is limestone, the so-called white stone in Russian terminology, consisting of nearly pure calcite. The admixtures of clayish materials (mainly of the class of hydromicas) constitute not more than 1-2% in it. This is the same white stone (limestone) that was commonly used for the construction of many cathedrals and churches in Moscow and other cities and towns. This limestone was extracted from quarries near the village of Myachkovo on the Moscow River and had thin porosity, pure chemical composition and softness, but was at the same time sufficiently strong.

In some fragments, apart from calcite, the following completion materials were found: gypsum, cement, etc. (the Table). Thus, the material of the fragment "the dragon's wing", as was shown by the analysis, is cement in whose composition gypsum, quartz and calcite were present.

An investigation of thin sections was made in order to compare the structure of limestone, taken from different fragments of the sculpture. It turned out that the material under investigation is finely porous detrital limestone, nearly fully composed by calcite. Calcite is present in the stone in the form of numerous petrified remnants of vegetable and animal origin.

The rock is composed by pelitomorphous calcite of an uneven lumpy structure. The rock is very porous, the porosity is not less than 10-12%. Pores are of an irregular shape, apparently original, between lumps of limestone. Weak recrystallization can be observed in some samples.

A detailed micropaleontological investigation was made of transparent sections, made of samples of various fragments of the sculpture, to determine the age and geographical origin of the stone. The analysis demonstrated that in some of them there were fusulines characteristic of only the upper strata of the Myachkovo level of the Moscow layer of the middle carbon - *Fusella* cf. *typica* Lee et Chen *extensa* Rauser, *Fusulina* sp. Consequently, the stone of which the sculpture of St. George the Dragon-slayer was carved, belongs to the variety of limestone out of a shallow Myachkovo quarry. An important result of the micropaleontological investigation was the finding of remnants of fusuline shells typical of limestone of the Myachkovo level both in the upper part (the torso of St. George), and in the fragments of the broken lower part of the sculpture (the leg and head of the horse).

Thus, it was shown that the fragments of the sculpture are identical both in a chemical and mineralogical composition, and in origin, on the basis of the X-ray phase analysis, petrographic and paleontological investigations. The authenticity of many lower fragments of the sculpture became indisputable thanks to the investigations conducted. It was decided to restore the famous monument of old Russian plastic arts.

The authors express gratitude to the paleontologist M.N. Solo-

vyova for her assistance in the conduct of the micropaleontological investigation.

The Table

The values of fundamental lattice spacings and intensities in the roentgenograms of stone samples

Sculpture fragment	Experimental data:			ASTM tables data:			card number:	Mineral
	d (Å)	J (%)	d (Å)	J (%)	d (Å)	J (%)		
1	2	3	4	5	6	7		
1. The torso of St. George	3.85	6	3.85	26	24-27			Calcite
	3.03	100	3.03	100				"
	2.83	3	2.83	2				"
	2.49	14	2.49	7				"
	2.28	18	2.28	21				"
	2.09	18	2.09	32				"
	1.90	20	1.92	4				"
	1.87	19	1.90	21				"
			1.87	42				"
	1.62	4	1.62	3				"
	1.52	3	1.51	2				"
2. The head of the horse	3.86	9	3.85	26	24-27			Calcite
	3.82	10						"
	3.04	100						"
	2.49	17						"
	2.28	25						"
	2.09	22						"
	1.91	34						"
	1.87	29						"
	1.62	7						"
	1.60	15						"
	1.52	13						"
3. The first leg of the horse	9.98	6	10.00	100	9-343			Illite, hydromicas
	9.40	6						
	8.12	4						
	6.45	4						
	4.47	4	4.47	80	9-343			Illite
	3.86	10	3.85	26	24-27			Calcite
			3.33	80	9-343			Illite
	3.03	100	3.03	100	24-27			Calcite
	2.49	19	2.49	7				"
	2.28	30	2.28	21				"
	2.09	25	2.09	32				"
	1.91	34	1.92	4				"
	1.87	38	1.87	42				"
4. The second leg of the horse	3.85	6	3.85	26	24-27			Calcite
	3.02	100	3.03	100				"
	2.83	3						"
	2.49	14						"
	2.27	18						"
	2.09	18						"
	1.90	20						"
	1.87	19						"
	1.62	4						"
	1.60	11						"
5. The dragon	3.84	5	3.85	26	24-27			Calcite
	3.02	100						"
	2.83	3						"
	2.48	14						"
	2.28	19						"
	2.09	18						"
	1.91	20						"
	1.86	19						"
	1.62	4						"
	1.60	11						"
6. The cuff on the left hand	14.73	2	15.00	100	13-135			Montmorillonite
	12.63	1	12.40	80	7-330			Illite-montmori.
	3.85	9	3.85	26	24-27			Calcite
	3.03	100	3.03	100				"
	2.83	3						"
	2.49	14						"
	2.28	20						"
	2.09	21						"
	1.90	16						"

1	:	2	:	3	:	4	:	5	:	6	:	7
		1.87		19								Calcite
		1.62		4								"
		1.52		8								"
7. The dra-	7.70		22		7.56	100		6-46		Gypsum		
gon's wing	4.29		65		4.27	51				"		
					4.26	40		5-490		Quartz		
	3.36		100		3.34	100				"		
	3.06		41		3.06	57		6-46		Gypsum		
					3.03	100		24-27		Calcite		
	2.88		24		2.87	27		6-46		Gypsum		
	2.68		15		2.68	28				"		
	2.50		7		2.49	7		24-27		Calcite		
	2.45		9		2.45			5-490		Quartz		
	2.29		7		2.28					"		
					2.28	21		24-27		Calcite		
	2.08		14		2.09	32				"		
	1.90		10		1.92	4				"		
	1.88		10		1.87	42				"		
					1.89	16		6-46		Gypsum		

Working Group 11

Theory and History of Restoration

Théorie et histoire de la restauration



TRIENNIAL OVERVIEW

Coordinator
E. v.d. Wetering
(The Netherlands)

Assistant Coordinator
H. Kühn
(Germany)

PROGRAMME 1985-1987

1. To inspire those working in the field of conservation and restoration in the broadest sense to a greater awareness that conservation and restoration are not mere technicalities but involve interpretation and considerations on various levels.
2. To widen the frame of reference as to the interdisciplinary approach in conservation and restoration; this more in particular as to fields of scholarship and science which may contribute fresh insights in establishing theoretical notions applicable to conservation and restoration, e.g., economics, theory of perception, psychology, different branches of philosophy, museology, etc.
3. To devote specific attention to theoretical consideration in the field of conservation and restoration of ethnographic materials, in particular with respect to objects pertaining to ceremonial and ritual functions that are still, to some extent, alive.
4. To stimulate the collecting of material concerning the history of conservation and restoration.

Some remarks on the functioning of the working group.

The working group for Theory and History of Restoration traditionally has been a very loose, ad hoc gathering of people during the triennial meetings. Other than with most working groups - where the cooperation between the members is more closely knit - this situation may be inherent to the subject of the working group. Each person in the field is somehow connected with theoretical problems of conservation and restoration. It is up to the coordinator to stimulate attention to certain areas and subjects; on the other hand he will always be confronted with surprising contributions from various, often unexpected, quarters. This may, on one hand, prevent the streamlining of the activities of the working group; on the other hand, however, it will generate unpredictable but potent new ideas. The repetition of old ideas, however, is by this procedure not always avoidable.



RESUME

PEINTURE, RESTAURATION, ET SOCIÉTÉ

Il faut risquer la question: "Qu'est-ce que la peinture?" La vie des tableaux exige que l'on s'intéresse aux origines de l'activité artistique et aux rapports de la restauration avec l'esthétique du temps.

Autour de l'art se structure un système, une trame d'intérêts économiques qui assurent la valorisation des oeuvres. Une esthétique de l'éphémère contredit le rôle du restaurateur.

Stefan C. Arteni (Inter-Society Color Council)
Myriam Sanchez-Posada de Arteni (Exhibition Conservator, The New York Public Library)
34-41 77th Street, #127
Jackson Heights, NY 11372

"...ce grand art universel et infini de la vraie peinture."
(Albert Dürer)

"Il ne s'agit pas de reproduire un objet mais, au sens ancien du mot, la vertu de cet objet," dit André Derain. C'est qu'il faut avoir la volonté de poser la question: "Qu'est-ce que la peinture?" Les mots valent par rapport aux mots. D'où la difficulté d'écrire du pictural. Pourquoi risquer cette question? Faut-il donc légitimer les oeuvres d'art ou la réalité du marché, des marchés de peinture aussi?

La mission de l'art est de construire un 'intérieur' contre l'espace planétaire externe. Cette idée de l'art exprime ce qu'Aristote nommait *âme* ou *entelequia*. La peinture est le plus hermétique des arts. Il y a une contradiction constitutive entre les signes manifestes et leur sens secret. La peinture est plus proche des hiéroglyphes que du langage.¹

Il existe un lien étroit entre les origines de l'art et la magie, le mythe et la religion. Les peintres de Lascaux avaient un but magique. C'est le prototype de l'activité artistique.² Freud a remarqué: "Les gens parlent avec raison de la 'magie de l'art' et comparent les artistes à des magiciens." Matila Ghyca disait: "La définition 'lato sensu' de la magie ira jusqu'à dire: tout ce qui libère une force, ou la capte...est un acte de magie. On peut aussi parler d'une 'relativité de la magie' et dire qu'une opération dynamique, captation ou émission contrôlée de forces, est toujours magique...pour ceux qui ne la comprennent pas." Dans le Rig Veda, *brahma* semble signifier 'hymne,' prière, formule magique, connaissance du sacré. On lit dans la *Chandogya Upanishad*: "En vérité, la personne est un sacrifice..." et aussi dans la *Brihad Aranyaka Upanishad*: "L'homme, en vérité, est un feu sacrificiel...Celui qui connaît la propriété...possède cette propriété. Sa propriété, en vérité, est le ton [de l'hymne]..." L'art est possession du sacré, l'art signifie rendre sacré. L'art est un langage symbolique.³

Il est certain qu'au XIXe et XXe siècles les rapports de l'homme et de la société subirent d'importantes transformations. Ortega y Gasset décrivait l'avènement des masses et l'intrusion des multitudes dans le domaine de la culture, un phénomène qui a influencé l'art de notre époque: en fait, depuis le XVIIIe siècle les hiérarchies sociales se sont transformées en une multitude informée, et le XXe siècle a vu naître les formes d'une culture de masse, qu'il s'agisse de la photographie, des films, ou de la télévision. Singulier phénomène, les masses seraient plutôt victimes que responsables des manœuvres commerciales leur imposant cette culture. La réhabilitation archéologique du passé - restaurateurs de tableaux, nombreuses éditions d'art, revues et journaux d'art, nombreux spécialistes - correspond à cette incertitude du public.⁴

La question de la restauration des tableaux a soulevé de tous temps d'âpres discussions. Le terme mériterait d'être précisé. Le problème, pour l'instant, est de rendre l'oeuvre d'autrefois à l'ardeur d'aujourd'hui et d'effectuer sans relais une prompte réappropriation. "Il ne s'agit pas de présenter les oeuvres... en corrélation avec leur temps, mais bien, dans le temps où elles sont nées, de présenter le temps qui les connaît, c'est-à-dire le nôtre," dit Walter Benjamin. Il nous faut attendre qu'on réunisse les matériaux nécessaires à construire une histoire de la sensibilité. Alors seulement pourrions-nous échapper à la tendance, si largement répandue, d'assimiler nos regards à ceux du passé.

Aspirant à se délivrer d'une liberté qui l'épouvante, l'homme se rue avec délice vers la servitude. Nous vivons une époque où la technologie désapprend peu à peu à l'homme de se servir de ses mains et de son cerveau. Sans aller jusqu'à affirmer que la technologie est la métaphysique de notre siècle, il est difficile d'ignorer les liens anciens entre l'art, les sciences, la magie et la religion. Mais voilà que, tout à coup, la science apparut comme le moyen d'interprétation des principes qui gouvernent nos vies. Ici ce n'est pas aux profanes que le restaurateur s'adresse, mais aux spécialistes. Il ne veut plus susciter une émotion artistique, mais il veut au contraire suggérer le thème d'une méditation: on peut faire la même constatation au sujet des fresques du Vatican où la restauration veut donner le sens d'un temps révolu et de l'éloignement historique, mais perçus à travers le filtre du progrès technique.

Cette interprétation se confirme encore si l'on songe que des données historiques permettent de supposer l'existence ancienne de peintres restaurateurs - voir les écrits du Docteur De Mayerne - et un des sujets les moins débattus devait sans doute être la notion des retouches. Rubens écrit au sujet d'un de ses tableaux envoyé à Florence: "Si c'est nécessaire, vous pourriez bien, ce que je vous permets volontiers, y mettre la main, et le retoucher là où le contretemps

ou ma négligence l'aura rendu nécessaire." La copie était un procédé courant et n'impliquait aucune fraude, notion encore impensée sur ce terrain. On n'ignorait pas les règles du nettoyage et on ne refusait pas de les appliquer. Mais il ne faut pas oublier que ces procédés veulent avoir un rapport logique avec l'esthétique du temps. "Lisez l'histoire et le tableau," disait Poussin.

On peut faire la même constatation au sujet des restitutions architecturales du XIXe siècle: c'est l'exemple du goût d'une époque, au nom d'une conception erronée de la 'vérité historique.' Ce qui est particulièrement frappant dans les récentes restaurations est le retour des controverses sur la valeur esthétique des vernis jaunés et des souillures. On sait que le jaunissement des vernis sert de filtre et protège les couleurs.⁵ Il faut relire les articles parus dans la presse pour comprendre le choc éprouvé par les littérateurs et critiques - leur influence est des plus problématiques - en présence de peintures nettoyées.⁶ En même temps, l'accord tacite entre artiste et restaurateur va se transformer en conflit.

Un des traits de l'esprit d'un âge déclinant est la prédominance du sens de la vue, prédominance qui semble être en rapport étroit avec l'atrophie de la pensée. Alors que la commercialisation de la culture, à travers les mass-media et la reproduction, s'étend, en rendant l'art accessible à un plus grand nombre, le niveau général des créations artistiques diminue. Il est indispensable de plaire au plus bas dénominateur commun. "A mesure que l'art s'enfoncé dans l'impasse, les artistes se multiplient. Cette anomalie cesse d'en être une, si l'on songe que l'art, en voie d'épuisement, est devenu à la fois impossible et facile," écrit E.M. Cioran. L'art des temps modernes - en commençant par les cubistes et les futuristes qui ont accueilli les nouveautés techniques à bras ouverts - est peu à peu devenu simplement un autre bien de consommation. Les courants naissent brutalement, se démodent dès qu'une autre tendance affleure et réveille les curiosités. La nouvelle société est mal préparée à découvrir un rôle directeur dans le goût. La valeur jadis accordée aux chefs-d'oeuvres a été remplacée par le prestige de la valeur commerciale. Gauguin disait: "Rien ne ressemble plus à une croûte qu'un chef-d'oeuvre." La technologie, les mass-media, ont réussi à dépouiller l'art de sa puissance iconographique.⁷

L'art du passé avait préféré la signification plutôt que la représentation, inventant des signes pour figurer, et non pour imiter. Les maîtres ne se souciaient pas de la logique des scènes qu'une seigneurie ou un clergé leur imposait. L'art, c'était la beauté des formes, des surfaces et des symboles expressifs. Gauguin disait que l'oeuvre d'art est une transposition, une caricature, de la pensée intérieure. Au-delà des imageries qui sont les obligations de la commande, chaque peinture affirme l'originalité par la façon dont elle est faite. Beaucoup se suffisent de l'image: à chaque génération, ils essaient de réduire la peinture à l'image, au récit, à l'idéologie. La représentation réaliste - soutenue par des doctrines politiques ou nationales - est allée jusqu'à tromper l'oeil; l'anecdote a remplacé le sujet, le signe est tué par l'amas de détails; c'est la peinture mimétique, la peinture comme miroir selon la République de Platon.⁸ Au-delà, il n'y a plus place pour la création mais seulement pour la mécanique insensible de l'objectif photographique. Les moyens techniques de reproduction sont bien plus fidèles et rapides. La représentation d'objets reconnaissables devient un masque qu'il faut arracher: elle fixe, en fonction de schémas convenus, la relation de la réflexion plastique à l'imitation des formes du monde. C'est la convention qui fixe. La valeur d'une oeuvre d'art ne se trouve jamais dans le répertoire d'imagerie mythique, religieuse, sociale ou politique, ni dans l'habileté d'un illustrateur.⁹ L'impressionnisme n'était pas seulement l'apparition d'une nouvelle technique; c'était avant tout, selon l'aveu de Renoir, un retour individuel vers l'esprit du grand art du passé. Une acceptation superficielle et partielle de l'impressionnisme, de la peinture claire, de la touche divisée, du paysage, porte à de nouveaux dogmes marquant l'art du XXe siècle. Oscar Wilde affirmait qu'un chef-d'oeuvre est une oeuvre sur laquelle se rencontrent le plus grand nombre de malentendus.¹⁰

Faut-il rappeler les querelles des images et le triomphe des iconoclastes chez les Byzantins, et la passion iconoclaste de la Réforme? Les Hébreux et les Arabes ont accordé à l'art un pouvoir réel pour interdire même la représentation des êtres vivants. L'art abstrait répond aux mêmes nécessités esthétiques et spirituelles que l'iconoclastie: refuser le sujet avec violence, c'est, en fait, croire au sujet, dans la mesure où on le redoute. Chaque fois que l'évolution des formes a atteint un certain matérialisme trop prépondérant dans l'oeuvre, aux détriment des valeurs spirituelles, comme au XIXe et même au XXe siècles, quelques artistes ont imposé une cure d'austérité.¹¹

Il faut parfois regarder la vérité en face. Autour de l'art se structure un système. L'art qui cherche d'abord à devenir une valeur commerciale, qui se soumet donc au culte du moment en compétition avec les mass-media, a créé des images creuses, en s'adressant à la surprise et à l'horreur, en citant hors-contexte les mythes anciens et les pseudo-mythes modernes, sous un barbouillage hâtif. Qu'appelle-t-on aujourd'hui la peinture? En somme, c'est du barbouil-

lage sans la forme, le sublime de la laideur. C'est un mode d'hallucination, où l'esthétique n'a rien à voir. On peut appliquer à la peinture ce que René Sudre, cité par Marc Havel, dit sur la musique: "L'esthétique repose sur l'interprétation de nos sensations... On vit nettement que les stimulations du diencéphale, siège des émotions, se faisaient à des niveaux différents: le parasympathique pour l'impression agréable, l'orthosympathique pour l'impression désagréable... on vérifie que l'accoutumance au désagréable est possible et qu'elle se traduit par une inhibition, dans les couches cérébrales supérieures, des réactions orthosympathiques. Cette accoutumance à la musique désagréable, qui peut abolir les réactions spontanées de la zone affective, peut même dépasser la mesure et changer l'intolérance en enthousiasme, comme on le voit parfois à notre époque, quand des causes personnelles ou sociales s'y ajoutent. On sait que le frein à des tendances affectives est un des moyens qu'emploie l'éducation de la volonté."

Des progrès augmentent sans cesse le nombre de produits qui permettent à l'artiste de sélectionner les vibrations lumineuses pour les rendre sensibles à nos yeux. Et pourtant c'est dans le domaine de l'art contemporain que l'on observe l'inconscience officielle qui semble accepter cette lamentable situation: les peintres 'les plus représentatifs de notre temps' sont aussi, trop souvent, ceux qui connaissent le moins leur métier. Aucune technique nouvelle ne semble se dégager des efforts de l'actuelle génération. Que ces formes d'art nous irritent ou nous satisfassent pleinement, nous n'en devrions pas moins étudier leurs moyens d'expression en toute sérénité. Les théories esthétiques, les idéologies, ne suffisent pas à créer de toutes pièces une technique nouvelle. Des 'hardiesses de métier' ont été maintes fois célébrées par une certaine presse avide de nouveautés puériles, qui feint d'oublier qu'il est facile d'innover dans l'absurde. La peinture est toujours en contact avec le système. Elle se lie à la trame d'intérêts économiques qui, outre sa valorisation et sa divulgation, semblent aussi servir de filtre qualitatif: lorsqu'on veut attaquer un artiste, on s'adresse à son marché et non à son oeuvre.

La vie des tableaux exige que l'on s'intéresse aussi aux relations intimes et réciproques avec le restaurateur. Il faut que l'on ne soit pas obligé tous les trente ans de soigner les peintures. Il est curieux de constater qu'à notre époque où la peinture est revenue à son point de départ, niant tout l'acquis des siècles passés, on assiste parallèlement à une résurrection extraordinaire des moyens de conservation. Tout n'est pas à admirer aveuglément dans le passé. Chaque peintre doit utiliser le matériau qui conditionne les effets qu'il cherche et la facture qui lui convient. A toute pensée esthétique convient un mode d'expression particulier. Mais n'oublions pas les paroles de Dufy: "Seule une belle matière peut être à l'échelle d'une belle idée. C'est cet équilibre qui nous donne l'émotion d'art." La conception esthétique est le point qui éclaircit ce contraste. Nous dirions plus encore: si le problème de la peinture avait été posé en termes de connaissance et non pas de commerce, il aurait peut-être conduit à des solutions, au lieu d'une peinture faite au nom d'un fatras d'idées qui se veulent révolutionnaires et qui pourraient bien n'être que l'obscur réaction d'une impuissance inconsciente.¹² "C'est le propre de toute forme parfaite que l'esprit s'en dégage de façon immédiate et directe, tandis que la forme vicieuse le retient prisonnier, tel un mauvais miroir qui ne nous rappelle rien d'autre que lui-même," disait Kleist.

Le risque que courent de telles oeuvres est de voir le temps altérer ces matières et ne plus laisser subsister l'accord tel que l'avait voulu le peintre à l'origine. Ce risque de l'éphémère est la conclusion normale d'une époque qui fit une si large part à l'improvisation. Il y a aussi un malentendu permanent, que nous avons déjà signalé, dans le fait que l'artiste accomplit une oeuvre périssable, tandis que le restaurateur devrait la conserver.

Avec le cinéma et la télévision, nous sommes arrivés au stade de la civilisation fondée sur l'image et transmissible par l'image. Malraux a mis en valeur la nouvelle fonction de l'oeuvre d'art: par un détour de leur destination d'origine on sépare ces objets de leur signification pratique et de leur contenu spirituel. Avons-nous affirmé ainsi l'autonomie de l'art? L'icone chrétienne était regardée comme un diagramme exprimant certaines idées; elle ne reproduisait pas des ressemblances terrestres. "La forme est la révélation de l'essence," disait Meister Eckhart. A nos yeux l'icone est devenue un assemblage de lignes et de couleurs. "L'abstraction sans aucun rapport avec l'humain n'est plus signe mais une arabesque," remarque Severini. L'esthétique byzantine et romane, par exemple, forme une phase dans l'histoire des expériences artistiques des peuples méditerranéens. Elle prévint une désintégration radicale de l'esthétique et des formes classiques, mais elle empêcha aussi un retour complet à l'esthétique classique. C'est Plotin qui envisage une connaissance totale et immédiate par la contemplation du noyau irrationnel enfermé dans la matière. On peut parler d'un langage artistique qui se sert de mots anciens pour les adapter à des structures grammaticales évoluées et tient compte des modifications phonétiques et sémantiques plus récentes.¹³ L'art vivant est devenu dès le XIXe siècle, par un processus de repli, un simple phénomène, éloigné des préoccupations et besoins pratiques - ou bien illusoires? - d'une société, dès

la disparition du système de mécénat, et fondé sur le rejet de l'art normalement accepté par un marché corrompu. Quand le langage artistique gréco-latin de la Renaissance bascule, en marge des courants et des noms qui les illustrent, il faut retenir des artistes qui ont joué un rôle considérable en dehors des théories. Campigli, Tosi, Morandi et Sironi, Derain, Dufy, Rouault et Villon, Juan Gris et Milton Avery, Marini, De Stael et Brancusi, atteindront au maximum d'expression plastique et de pureté. Ces isolés font figure de héros et de martyrs. Matisse écrivait: "Les moyens les plus simples sont ceux qui permettent le mieux au peintre de s'exprimer. S'il a peur de la banalité, il ne l'évitera pas en se représentant par un extérieur étrange, en donnant dans les bizarreries du dessin ou les excentricités de la couleur..."¹⁴ On a essayé de lier la peinture aux évolutions sociales et aux conceptions idéologiques. Il n'en faut pas conclure que les formes de l'art dépendent exclusivement de ces facteurs. Au terme de cette remontée aux sources, le problème reste entier, ou tout au moins entouré d'une épaisse frange d'indétermination. Le dernier mot n'est pas dit. On ne peut prédire l'avenir de la peinture. Puisque l'art se doit d'être la plus haute incarnation de l'individu, il faut qu'il invente un vocabulaire neuf. L'issue, pour l'art, ne peut être que dans un retour vers le signe, mais un signe qui ne renie pas l'homme. Peut-être celui qui ouvrira la nouvelle voie est-il déjà parmi nous.

PROPOS TECHNIQUES. L'EAU ET LA PEINTURE A L'HUILE

Sous des formes variées, l'union de l'huile et de l'eau se trouve présente pendant des siècles. L'huile était traitée sous l'action de la chaleur et de produits basiques siccativants (poudre d'os, litharge, verre de Venise et plomb) puis décolorée au soleil. Les agents mouillants ou dispersants employés par les maîtres sont les savons: ceux à vase de chaux ou de plomb que l'on trouve dans les huiles cuites. Presque toutes les recettes du manuscrit du Docteur De Mayerne comportent de la litharge. La réaction du plomb sur l'huile forme une espèce de savon qui donne aux pâtes une consistance beurrée et maintient la structure de la touche. L'emploi judicieux des huiles cuites provoque un séchage en profondeur progressif sans changement de ton ni embus. On peut travailler en s'aidant d'un peu d'essence. De Mayerne observe: "L'addition de l'huile d'aspic au blanc & au bleu, qui fait qu'ils ne meurent jamais, ce que je répète parce que c'est un grand secret..."

L'eau, entraînée par la brosse, confère aux pâtes une extraordinaire ductilité. "Les paysages s'esbauchent avec broisses de poil de porc les plus déliés...lesquelles quand on intermet le travail se mettent dans l'eau de peur qu'elles ne seichent. Si elles se seichent, il ne faut que les laver avec le savon mol, & elles sont aussi bonnes que jamais."

"Devant que mettre vos pinceaux dans l'huile, il les faut tremper dans l'eau un quart d'heure, ainsi ils seront plus doux & plus aisés à manier."¹⁵

Cette action est particulièrement nette avec le blanc d'argent. Le blanc d'argent joue le rôle de dispersant. Notons ce conseil de De Mayerne:

"Blanc de Plomb soit premièrement broyé avec eau, puis estant sec avec huyle. Si vous le mettez deux ou trois fois au soleil couvert d'eau, il devient beaucoup plus blanc, comme on blanchit le linge. Soit toujours dans l'eau."

"Toutes couleurs se peuvent garder broyées avec eau, & seichées, & se destremper seulement avec huile quand on en veult user sur la palette, hormis le Blanc de plomb qui estant dans l'eau devient toujours plus beau."

Marc Havel remarque: "L'émulsion d'un peu d'eau aux couleurs à l'huile rend la pâte courte et crémeuse, facilite les superpositions instantanées et nettes, les modelés onctueux." Le travail dans le frais (*alla prima* - voir les propos de Van Dyck) donne une matière homogène. Le séchage reste lent, mais le matériau, thixotropique, permet la superposition. Empiriquement, les anciens peintres ont su réaliser des produits thixotropiques. L'important, c'est le traitement de l'huile avant utilisation. On introduit dès le début un siccativant. Contrairement à l'opinion courante, sa présence n'entraîne pas des craquelures. Le peintre aura disposé de pâtes souples et crémeuses, se superposant facilement, gardant la touche et permettant de travailler rapidement. A éviter mat sur brillant et brillant sur brillant: "Quand on met une seconde couche de couleur sur la première qui reluit, aussi tost qu'elle est seiche, incontinent la couleur s'emboite et ne meurt point."

Mat sur mat est la technique des couleurs à l'eau. Brillant sur mat répond à la règle 'gras sur maigre.' Les formules les plus simples sont les meilleures. Plutôt que les compliquer par des temperas ou émulsions diverses, mieux vaut tirer parti des possibilités de l'huile cuite et de l'émulsion d'un peu d'eau.

Peut-être cette curiosité toujours en éveil, cet appétit de connaître, qui fut un des ferments de l'art moderne, sera-t-il aussi une des raisons de sa perte. On a trop facilement oublié les procédés anciens: l'angoisse du métier perdu était en réalité la cause de l'impressionnisme. Malheureusement, les peintres étaient désormais livrés à leurs propres forces.

NOTES

1. "Se rappeler qu'un tableau - avant d'être un cheval de bataille, une femme

nue, ou une quelconque anecdote - est essentiellement une surface plane recouverte de couleurs en un certain ordre assemblées." Maurice Denis marque la priorité de la couleur, non une exclusive. Sur le plan philosophique, il s'agit d'un art qui s'exprime en un langage spécial, celui des équivalences.

2. Cassirer écrit: "Dalla concreta corporeità materiale, a cui inizialmente il culto è legato, il pensiero religioso e l'intuizione religiosa si innalzano sempre più alla pura forma immaginativa. Siccome in essa, soprattutto in essa, si vede la garanzia per la conservazione dell'io, oltre la mummia, mezzo ugualmente efficace per l'immortalità diventa la statua. Da questa fondamentale concezione religiosa si sviluppa l'arte figurativa, particolarmente la scultura degli Egiziani."
3. Voir Ananda K. Coomaraswamy: "...for the East, as for St. Thomas, *ars imitatur naturam in sua operatione*...It is of the essence of art to bring back into order the multiplicity of Nature, and it is in this sense that he [the artist] 'prepares all creatures to return to God'...art is by definition essentially conventional; for it is only by convention that nature can be made intelligible, and only by signs and symbols...."
4. Informare: le verbe latin signifie façonner, former.
"Il bisogno pratico, che è nel fondo di ogni giudizio storico, conferisce ad ogni storia il carattere di storia contemporanea, perché, per remoti e remotissimi che sembrino cronologicamente i fatti che vi entrano, essa è, in realtà, storia sempre riferita al bisogno e alla situazione presente, nella quale quei fatti propagano le loro vibrazioni," écrivait Croce.

Voir aussi Ortega Y Gasset: "La restauración histórica es siempre una ficción: en ella se cubren los hechos pasados de un barniz que les da esa brillantez aparente, propia de las cosas actuales. Además, en la restauración histórica, lo que importa es el pasado y su aproximación a nosotros."

"Sur le plan absolu, ces livres avec des reproductions en couleurs sont absurdes, on n'a jamais le ton et encore moins la matière..." écrivait Nicolas de Stael. Victor Hugo avait prévu l'effet de l'imprimerie sur l'art: "Le livre de pierre, si solide et durable, allait faire place au livre de papier...L'imprimerie tuera l'architecture." Le cinéma qui a permis la reproduction du mouvement, les différents points de vue et les sauts dans le temps, et enfin la télévision, peuvent influencer tous les domaines de l'existence et ils ont forcément affecté l'art. Ils ont conduit à une crise.

5. Voir l'article de Gunter Essers, *Maltechnik Restauero*, no. 4, Octobre 1986.
6. "...the recent restoration of certain important paintings in Italy and Spain...has not only altered the aesthetic appreciation of these works but has in some ways changed our conception of the artists who made them. In the end, the history of European painting will very likely be somewhat revised," écrit Jack Flam, *Connoisseur*, Mars 1986.

A ce propos voir les articles critiques de Grace Glueck, "Masterpieces Rise and Fall on a Tide of New Expertise," *The New York Times*, 7 Décembre 1986; Olivier Bernier, "Venice Reclaims its Glory from the Ravages of Time and Tide," *Ibid.*; Alexander Eliot, "Art Restoration, So-Called," *The New York Times*, 12 Décembre 1986; Roberto Suro, "Saving the Treasures of Italy," *The New York Times*, 21 Décembre 1986; Mary Davis Suro, "The Sistine Restoration: Trouble in Paradise," *The New York Times*, 4 Janvier 1987.

Voir aussi Mark Evans, "Critics' Mistakes, Prejudices Come Back to Haunt Them," *New York City Tribune*, 18 Février 1987: "If history has often reversed critics, and their expertise is questionable, how objective are they? The answer, of course, is not at all. Virtually no one studies to become a critic...Critics...are concerned with their own place in history...today's critics...tolerate anything they can label avant-garde...."

Les restaurateurs du Vatican ont réfuté les arguments des critiques et historiens de l'art. Voir U.P.I., "Sistine Chapel Restoration Under Fire," *New York City Tribune*, 17 Février 1987.

7. "If consumers in a certain field do not seek the highest quality of whatever is produced or created, or even cannot tell the best from the poorest quality, free enterprise tends towards the poorest, since the poorest is easier and cheaper," écrit Lev Navrozov.

Voir aussi Ortega Y Gasset: "Es erróneo suponer que un simple aumento de posibilidades multiplica las voliciones. El 'nuevo rico' no sabe qué querer: de aquí su falta de originalidad en las adquisiciones que hace, la mayor parte de ellas sin apetito verdadero. Se orienta en los deseos de los demás y compra lo que otros querrián."
"...Ciertamente vago internacionalismo ha pretendido ligeramente nivelar con un

conjuro caprichoso e inválido la diferencia entre las naciones, e impulsado por lunáticas inspiraciones ha urdido una pseudocultura en que se fingia ignorarlas."

"Mais désirer juste, voilà un grand art, ou plutôt un don," disait Kierkegaard.

"Transvaluation of all values is the most fundamental character of every civilization...It begets no more, but only reinterprets...." écrivait Spengler.

8. Comparez les symboles de l'Inde et les photographies pornographiques. Voir Albert Aurier: "Dans la nature, tout objet n'est en somme qu'une idée signifiée."
9. Le trait pose sur la feuille la tension interne d'une forme et jamais son enveloppe.

Voir Ghyca: "La vision n'est pas instantanée: c'est une opération composée du raccordement d'images successives et à mesure que l'oeil se lève par exemple pour examiner la façade verticale d'un édifice, il y a non point un plan vertical de projection, mais une série de plans non plus verticaux, mais perpendiculaires aux axes momentanés de vision...qui donnent par cette vision 'optico-physiologique' (qui se passe aussi bien dans le temps, ou plutôt la 'durée', que dans l'espace) une image composée du raccordement des projections fragmentaires en ces plans tournants dont l'enveloppante est une surface courbe, cylindrique, ou plutôt sphérique, si l'on admet le même phénomène pour la vision horizontale: l'oeil doit tourner de gauche à droite...."

10. Le New York Times cite Verdi: "Let us return to the past: it would be progress."

La peinture des impressionnistes, bien que claire, n'est pas lumineuse. Eclaircir un ton avec une pointe de blanc consiste à l'opacifier. C'est pourquoi un noir opaque ne paraît jamais profond. Plus l'opacité sera grande, plus la couleur apparaîtra claire, mais aussi moins pure, moins différenciée de ses voisines. C'est le cas des embus et de la peinture à l'huile mate. Les complémentaires constitueront un moyen, peut-être approximatif mais commode, de s'exprimer en couleur-valeur, mais l'addition des complémentaires ne peut donner qu'un gris.

11. La peinture n'est qu'un moyen de transmettre les choses de l'esprit. Les couleurs constituent un langage. On se souvient de Taine: "Une gamme de couleurs ne figurant aucun objet réel peut-être riche ou maigre, élégante ou lourde." Le même mot 'couleur' désigne la pâte siccatrice qui sert à peindre (un pigment au sein du liant) et aussi notre vision d'une surface colorée, la touche de peinture. La recherche de la couleur comporte et implique le souci du métier, car il est impossible de séparer matière et couleur, et la matière est fonction du métier. Le cercle chromatique de Paul Sérusier n'est assimilable à aucun des types connus. Dans son empirisme, une figure où il s'agit de couleurs matérielles a une signification certaine: on peint avec ce qui est disponible sur la palette. La conscience très nette que Paul Sérusier avait de la symbolique des couleurs et des formes le rapproche des Anciens: c'est un système de lois aux ambitions aussi métaphysiques que scientifiques. L'harmonie des couleurs évoque l'harmonie des nombres et la musique. "Les couleurs sont la musique des yeux," disait Delacroix. Un des élèves de Sérusier, devenu bénédictin, le P. Verkade, confronte ses doctrines avec la pensée du style, de ceux qui croient que l'art a à faire avec la révélation.
12. Ghyca cite J. Mac Murray: "Une oeuvre d'art est anatomiquement quoique non physiologiquement, un organisme. C'est une harmonie, une unité." Et il cite aussi S. Alexander: "L'oeuvre d'art est en premier lieu un être concret individuel, imposant l'impression de posséder une individualité propre comme une personne...son critérium est précisément l'unité qu'elle montre dans la variété de ses parties, son caractère organique, le fait de manifester un dessein."

Voir aussi Ortega Y Gasset: "Cuando hay crisis sustantiva de una cultura? La cultura, rigurosamente hablando, es el sistema de convicciones últimas sobre la vida; es lo que se crea con postrema y radical fe sobre el mundo. Esta fe puede ser científica o no, religiosa o sin Dios."

Pourtant, on a déjà rejeté le mythe de la technologie, des mass-media et des sciences. On tient presque partout la technologie pour responsable de la plupart des maux. On ne fait plus confiance aux procédés et aux produits industriels, ni aux institutions qui profitent de leur commerce: partis

politiques, gouvernements, marchands, spécialistes. On ne fait plus confiance aux historiens et critiques d'art.

"The new art...expects only one thing of its viewers - that they know the difference between good and bad, and choose the latter. 'Bad' art shifts the burden of looking at art to looking at presentation...." écrit Paul Taylor, *Art News*, Avril 1986.

Voir aussi Paul Taylor, "How David Salle Mixes High Art and Trash," *The New York Times*, 11 Janvier 1987; Donald Kuspit, "'What It Is' at Tony Shafrazi," *Artscribe*, Janvier-Février 1987: "The only thing to do with such a large group exhibition is to imagine that all the works are by one artist. In this case, his name is 'charlatan.'"

"In rapporto alle esigenze della conservazione ci si chiede a volte...fino a quale livello...di raffinatezza tecnologica dovrà arrivare una galleria d'arte per far fronte in concreto alle eterogenee esigenze dei materiali con cui sono realizzati quadri...contemporanei," écrit le restaurateur Enzo Pagliani, *Arte*, no. 168, Novembre 1986.

13. Les anciens peignaient très coloré. "La forme et le dessin, écrit Gauguin, peut exprimer tout et cela noblement soit par la ligne exclusivement, soit par des tons qui modèlent et par suite simulent la couleur...Mais pourquoi à de belles formes ne pas ajouter un autre élément, la couleur?"
"Le dessin et la couleur ne sont pas distincts, dit Cézanne à Emile Bernard. Au fur et à mesure que l'on peint, on dessine. Plus la couleur s'harmonise, plus le dessin se précise. Quand la couleur est à sa richesse, la forme est à sa plénitude." Cette glorification de la couleur n'est pas sans rappeler l'esthétique byzantine et vénitienne où la couleur et la lumière représentent la splendeur du monde divin. C'est un des thèmes éternels des arts plastiques.

14. "La bonne peinture est dévote par elle-même," disait Michel-Ange.

Modigliani écrivait: "Je peins pour élever les hommes."

La véritable magie de l'art vivant tient à ce qu'il est hors du temps. Schopenhauer écrivait: "La grande gloire de la peinture est de pouvoir fixer dans un tableau un monde éphémère composé d'événements particuliers, en constante transformation mais qui pourtant donne l'idée d'un tout et la sensation du temps, tout en paraissant l'arrêter puisqu'il élève l'individu au rang de symbole [ou d'archétype, dirons-nous,] de l'espèce."

"La forme stylistique nécessite, pour être comprise, de la matière des formes réelles," disait Ortega y Gasset. Chaque civilisation a trouvé une écriture personnelle. Nous sentons bien que nous sommes actuellement au bout de toutes les routes.

15. Voir J.P. Jouffroy, *La mesure de Nicolas de Stael* (Neuchâtel: Ides et Calendes, 1982) p.52: "Chez Cézanne la brosse sèche en soie de porc, à peine assouplie, avant son premier usage, par un petit bain de Diane dans l'eau tiède."



SUMMARY

The following treatise examines a restoration, in the modern sense of the word, carried out at the end of the 15th c. of mediaeval wall-paintings in Macedonia.

THE RESTORATION OF THE WALL-PAINTINGS IN THE CHURCH OF ST. NIKITA AT ČUČER/MACEDONIA IN 1483-1484

Ivan Bentchev

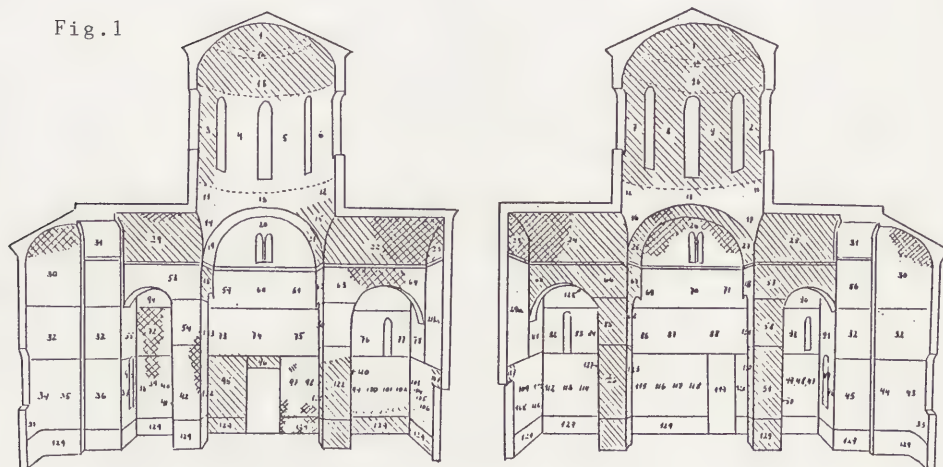
Rheinisches Amt für Denkmalpflege
Abtei Brauweiler
Ehrenfriedstr. 19
5024 Pulheim/Brauweiler
West Germany

The complete decoration of the Church of St. Nikita at Čučer near the Macedonian city of Skopje (fresco on plaster) has been identified by signatures as the work of the important Byzantine painters Michael and Eutychios who were responsible for many frescoes which have survived in Serbia and Macedonia. Miljković-Pepel¹ considers 1313/15 as the date 'ante quem non' of the original paintings. In his view, it was only after the decoration of the church at Staro Nagoričino that these paintings were undertaken, i.e., after 1318. Horst Hallensleben² does not quote a precise date for the creation of the original paintings but designates them as the preliminary stage for the painting at Nagoričino (1316/17) and associates them with the "Master of the Passion" who was active there.

Additions and entire figures and scene of a later date can now be detected in the frescoes of the church, even by a layman. From an inscription over the South Portal in the Slavonic language (Fig. 2), we know that this restoration was performed in 1483/84. The inscription and the date were first published by G. Millet³. Svetozar Radojčić⁴ concurred with Millet in his opinion and postulated that the restoration work followed damage caused by the Turks in the late 14th c. or during the first half of the 15th c. H. Hallensleben presumed that a collapse of the vaulting necessitated this work. I believe that the paintings had been damaged by the earthquake of 1473⁵.

Radojčić correctly concludes that the painters who in 1483/1484 restored the frescoes at St. Nikita's in a manner which appears astonishingly modern - as will be noted below it is entirely a question of additions on new plaster and only in one case has a figure been painted out (No. 95) - were responsible for the paintings in the following churches: Treskavac monastery (1483), the church of St. Nikola Bolnički at Ochrid (1480/90), the church of St. Nicholas of the Nun Eupraxia in Kastoria⁶ (1486) and the church at Poganovo (1499). The characteristic works of these painters in the churches mentioned - a list of their paintings in the Greeks area has been compiled by A. Xyngopoulos⁷ - display clear elements of the Milutin School (1st half of 14th c.) which, according to H. Hallensleben⁸, can only be explained by the paintings they had completed prior to this date at St. Nikita's (i.e., 1483/1484). These painters not only piously restored the damaged frescoes of their predecessors, they also carefully studied the old style so that the additions could be accurately matched in style and colour, precisely in

Fig. 1



- original paintings, 14th c.
- ▨ restoration-additions-, 1483-1484; 1, 1a, 1b: 19th-20th c.
- ▩ damaged paintings

the manner of modern restorers when confronted with the task of retouching a damaged painting without painting over the original. Impressed by the skill of the old masters, these restorers subsequently adopted the old style in many cases and copied them in new works. However, I believe that the restorers of St. Nikita's were also responsible for painting over the wall-paintings in the chapel of St. Nicholas in the church at Kuceviste (1501, according to the inscription). The original first layer, partially uncovered by Yugoslav restorers in our time, reveals the identical pattern of the grain effect of the base zone as in the church at Decani (1335-1350). The restoration work at St. Nikita's - application of new plaster to the damaged area and its repair *al fresco* as illustrated by the example of Kuceviste - cannot be explained at all by the painting technique. The painters of c. 1500 were able to paint *al fresco* and *al secco*.

The work of restoration of 1483/84 at St. Nikita's has attracted the attention of a number of researchers. The most intensive work on this subject has been carried out by Miljkovic-Peppek and Hallensleben. The following investigation and compilation, which retains the scheme of Miljkovic-Peppek⁹ and his listing of the pictures, permits an accurate distinction to be made between the original paintings and the additions of 1483/84 (Fig. 1).

Cupola and tambour

1. C. Pantokrator: 19-20th c.; Miljkovic-Peppek: 19th c.; Hallensleben: 20th c. Miljkovic-Peppek is of the opinion that it was originally the Heavenly Liturgy which was painted here since the space between the Apostles would be large enough for this and the Medallion Christi which is from the original (or second) restoration is already there.
- 1a MS of 19-20th c.
- 1b Heavenly Liturgy: 19-20th c., ikonographically similar to the same scene in Nerezi dating from 20th c.
2. The Prophet Isaiah
3. The Prophet Jeremiah
5. The Prophet Elijah
7. The Prophet Samuel: 20th c.
8. The Prophet Avdias
9. The Prophet Ezekiel

It seems that these five prophets, of a total of eight in St. Nikola's, have been restored, partly in the 19-20th c., partly earlier.



Pedentive

15. St. Mark the Evangelist

Additions in the 15th c. from the feet upwards, also the architectural decoration on the right.

Principal feasts

18. Proclamation

The Archangel Gabriel in the left part has been added almost entirely on new plaster in the 15th c.

The right part (Mary) belongs to the original decoration.

21. The Baptism of Christ: only the lower right corner of the scene has been added. At the edge of this new area, there is a crack which runs from the shoulder of the angel on the right, across the left arm of Christ and downwards to the left to the personification of the Jordan. The addition accounts for almost a quarter of the entire scene.

22. Glorification: The scene has suffered considerable damage. Only the left side (Moses, hilly landscape on the left, St. Peter and the apostle in the centre).

24. Entry into Jerusalem: 15th c. The right half of the scene survives, showing a group of Jews.

25. Crucifixion: 15th c. painting on new plaster.

28. Ascension: 15th c. painting on new plaster.

29. Pentecost scene: 15th c. painting on new plaster.

For scenes N 22, 23, 24, 25, Miljković-Pepek states that these are "probably compositions which have been painted over or damaged". "Probably Glorification, Resurrection of Lazarus, Entry into Jerusalem and Crucifixion". In our opinion, the Crucifixion is an original scene which has not been restored. The Glorification is indeed damaged in the upper area but it is also part of the original painting.



Fig.3

Miljković-Peppek's opinion that the scene of Christ in limbo is painted on new plaster has not been confirmed by examination either. The scene is badly damaged but dates from the 14th c. The head and part of the apparel of Christ and two angels in heaven have survived.

Cycle of Christ

- 65. Christ before Pontius Pilate: 15th c. on new plaster.
- 66. The Scorning of Christ: 15th c. on new plaster.
- 67. Golgotha: 15th c. on new plaster.
- 68. Death of Judas: 15th c. on new plaster.

Cycle of the Miracles of Christ

- 83. The Driving-Out of the Demons: 15th c. on new plaster.
- 85. The Healing of the Blind Shepherd: 15th c. on new plaster.

Lower zone of the Naos

- 95. John the Baptist (Fig. 2): entirely on new plaster. Painting from the 15th c. This is the only place where a large area of existing painting has been plastered over and repainted. The new plaster starts 10 cm away from the left corner of the wall and encloses the base and accompanying strip and the Slavonic inscription top right. Miljković-Peppek speaks only of "largely overpainted" which is not correct.
- 96. Greek and Slavonic inscription on the renewal of the church¹⁰: (Fig. 2)
 "Use the thought of death for living.
 Through the revelation of the Father and through the continuation of life and through the perfection of the Holy Ghost.
 This Divine Church of the Holy Martyr Christi-Nikita was renovated in the course of 1483-1484".



Fig. 4

97. St. Demetrios (Figs. 2, 4): only the head and the nimbus have been added on new plaster.
- 101, 102. St. Pantaleimon and St. Damianos: the lower parts of the apparel have been painted over.
103. St. Athanasios of Athos: the lower part of the apparel has been painted over.
104. St. Anthony: the lower part of the apparel has been painted over.
105. St. Paul of Tiva: the lower part of the apparel and the lettering to the right of the head has been painted over.
106. St. Anthony the Great: the lower part of the apparel has been painted over.
107. Ornamental rectangle with floral motives above the West Portal. 15th c. Miljković-Peppek leaves open the question of date here. The floral motives are clearly identical with the later redecoration of the base zone of the pillars and, in part, of the walls (floral frieze above the simulated marble).
108. St. Eutymios: head added, also the inscription and the lower part of the apparel.
121. St. Peter the Apostle: addition on new plaster from the shoulders downwards (Figs. 2 and 3).
122. The Archangel Michel: addition on new plaster from the shoulders downwards (Figs. 2 and 3).
123. St. Nicholas: addition of the 15th c.
125. St. Paul: addition of the 15th c. from the knees downwards.
126. The Archangel Gabriel: addition of the 15th c.
127. St. Mina: addition of the 15th c.
- 127a St. Kyrikos: addition of the 15th c.
128. Saint in monk's habit: addition of the 15th c.
- 128a The Prophet Solomon: addition of the 15th c.
129. Base zone with painted graining (Figs. 2, 3): 15th c. pillars left and right of the South Portal and left of the West Portal. South side of west wall and west side of south wall (the south-west corner).

References

- 1 Petar Miljković-Peppek, *Deloto na zografite Michajlo i Eutychie - L'oeuvre des peintres Michel et Eutyche*, Skopje (1967), p. 53.
- 2 Horst Hallensleben, *Die Malerschule des Königs Milutin*, in: *Die Monumentalmalerei in Serbien und Makedonien*, III, *Osteuropastudien*, Reihe II, 3-5, Gießen (1963), p. 53.
- 3 Gabriel Millet, *L'école grecque dans l'architecture byzantine*, Paris (1916), p. 12; W. Sas-Zaloziecky, *Die byzantinische Kunst in den Balkanländer*, München (1955) p. 125; Vladimir R. Petković, *Pregled crkvenich spomenika kroz povescnicu srpskog naroda*, Beograd (1950), p. 212.
- 4 Svetozar Radojčić, *Jedna slikarska skola iz druge polowe XV weka*, *Zbornik za likovne umetnosti*, I, Novi Sad (1965), pp. 64-104.
- 5 D. Perlović, R. Marinković, *Iz nase knizevnosti feudalnog doba*, Beograd (1975), p. 92.
- 6 Pelekanides, Kastoria, I. Thessalonike (1953). fig. 179-188.
- 7 A. Xyngopulos, *Exediasma istorias*, Athen (1957), pp. 61-93.
- 8 H. Hallensleben, op. cit., p. 30.
- 9 P. Miljković-Peppek, op. cit., fig. VII, VIII.
- 10 Translation Prof. Dr. Erich Trapp, Bonn.



SUMMARY

The Conservator occupies an uncertain position in the Art World. His interventionist role challenges the intense relationship with objects fostered by the romantic imagination and cherished by Arts Professionals, ie. curators, Administrators, art historians, dealers and critics.

Moreover the implications of conservation are potent reminders of the instability of our accumulated heritage, which as we turn increasingly to the past for reassurance, makes the security of refuge from the present offered by the 'patina' of age.

So the conservator is an isolated figure, belonging neither to Art nor to science, nor to precisely past or present; he is the Jeremiah of the Art world.

THE ISOLATED CONSERVATOR

Laura Drysdale, Freelance Conservator

PART 1 - THE ART WORLD: CONSERVATION'S CONTEXT

1. The Profession of Conservator

The area to be discussed here, that is the Conservation of artefacts, the 'movable heritage', is but a small part of the spectrum of potential interpretations of the word. It is in philological competition with the care of landscape, of wildlife, even, according to the 'Oxford English Dictionary', with 'the preserving of fruit or the like'. The conservator, that is the person who performs this preservation, has a specific task whose terms of reference have been delineated in true supra-natural form by ICOM (The International Council of Museums) in its document 'The Conservator-Restorer, A definition of the profession.'

"The activity of the conservator-restorer consists of technical examination, preservation, and conservation/restoration of cultural property:

Examination is the preliminary procedure taken to determine the documentary significance of an artefact; original structure and materials; the extent of its deterioration, alteration, and loss; and the documentation of these findings.

Preservation is action taken to retard or prevent deterioration of or damage to cultural properties by control of their environment and/or treatment of their structure in order to maintain them as nearly as possible in an unchanging state.

Restoration is action taken to make a deteriorated or damaged artefact understandable, with minimal sacrifice of aesthetic and historic integrity.

Conservators-restorers work in museums, in official heritage protection services, in private conservation enterprises or independently. Their task is to comprehend the material aspect of objects of historic and artistic significance in order to prevent their decay, and to enhance our understanding of them (so as to further the distinction between what is original and what is spurious). (1)

This conveys a rather more elevated view of the job than might be appropriate to, for example, the interminable cleaning of cuniform tablets by one man in the British Museum, and it could have been more elegantly phrased. The definition does however draw attention to the absolute primacy of that focus of the conservator's vision, the artefact - or in conservator-speak, **The Object**.

2. The Church of Art

"LOUISE DUBEDAT: I believe in Michael Angelo, Velasquez and Rembrandt; in the might of design, the mystery of colour, the redemption of all things by Beauty everlasting and the message of Art that had made these hands blessed. Amen."

Bernard Shaw (1906) The Doctors Dilemma

Maurois observed that American's Museums were their cathedrals, their contents contemporary ikons, to be run by a priesthood and worshipped by a congregation. This image is equally applicable to Eastern and Western Europe. We have only to turn it on its head to recognize its validity, since churches in the Soviet Union are presented by the State as institutions of sociological and aesthetic education, while conversly objects imbued with Soviet achievement are displayed in quasi-religious style. Lenin's tomb is clearly a place of pilgrimage; it is a reliquary inside which lies the ultimate object.

This supplanting of religion by the State holds a mirror to our own practice. Taking a collection is interchangeable from Ely Cathedral, should you wish to partake in secular worship, to the Victoria and Albert Museum where it is posited as a donation of conscience.

The analogy is infinitely extendable since it is a tenet of contemporary liturgy that materialism, faith in objects, has

supplanted christianity as the State assumes to itself functions - social worker/vicar for example - hitherto held by the church.

3. The Christly Artist

Raymond Williams has drawn attention to the development of the notion of Art as the seat of imaginative truth which was expressed by the Romantics in the late 18th Century. But the equation of Christ with the Artist was already implicit in Renaissance claims for the intellectual status of the painter and sculptor by, among others, Leonardo; Durer's self portraits make it explicit. Wordsworth saw the poet and artist as

"an upholder and preserver, carrying everywhere with him relationship and love." (2)

Thus the artist is the one who has access to an ideal of human perfection, our bulwark against

"the disintegrating tendencies of the age." (3)

This Romantic view of the Artist has been shown by Raymond Williams and more specifically by Nicholas Pearson, (4) to have deeply influenced the State's dealing's with the arts. Keynes' interpretation of the Artists's social position allowed the emergence of the Arts Council of Great Britain as a responsive rather than initiatory body echoing the strange 'otherness' of its constituents.

"The work of the artist (is) individual and free, undisciplined, unregimented, uncontrolled. The artist walks where the breath of the spirit blows him. He cannot be told his direction; he does not know it himself." (5)

Such romanticism is as applicable retrospectively. Waldemar Januszczak's vociferously stated objections to the Cimabue crucifix being exhibited at the Royal Academy after Conservation (a show sponsored by Olivetti) neatly encapsulates the issues: (6)

(1) The Crucifix is the most potent representation of a point when Western Civilization began to free itself from medieval superstition. The synthesis of the figure of Christ and its depiction of Cimabue, a **named** artist, makes its 'hijack by the entertainment industry' (blockbuster exhibition) heretical.

(2) The hand of the Master, Cimabue, has been obscured by the Scientific Methodology employed in its Conservation. Modern man's hubris permits the crucifixion of the Crucifixion by unfeeling reason (Roman Law).

(3) The Ikon is being treated with disdain 'just to sell typewriters'. Associating commerce with art is as offensive to Mr Januszczak as the money lenders in the temple were to Christ.

(4) The Crucifix is thus besmirched by the sins of lust, pride and avarice, with the other four, intemperance, envy, sloth and ire reverberating in the undertow of his hellfire denunciations.

4. The Paternal Establishment

The Christly figure of the artist is balanced in this artist/object/establishment trinity by the paternalism of his patron. That is to say by the gravitas of the State, its institutions and functionaries. As Pearson says:

"The visual arts have traditionally and historically reflected the interests and tastes of small and powerful sections of society. These classes have tended to universalize **their** tastes, experiences and culture as being the culture of **the** nation." (7)

Indeed our national museums owe their existence to private initiative by rich and/or powerful men. The collections of Sir Robert Cotton, Robert Harley Earl of Oxford and Sir Hans Sloane form the basis of the British Museum as created by the Pelham Government in 1753. The Victoria and Albert Museum was largely the inspiration of its first director Henry Cole, supported by Prince Albert. To quote Pearson again:

"The relationship of private initiatives and activities to State power and authority is very important, particularly in Britain where so large a part of the work of government is vested in semiautonomous bodies and organizations, and where State power is split between a series of interrelated agencies and institutions under the overall authority of the Crown." (8)

Before considering the nature of the State's involvement in

'cultural property', I want to reaffirm the metaphor of museums as contemporary churches whose contents have a quasi-spiritual authority. Cole himself in a speech to students at Nottingham School of Art three months before his retirement declared a vision of the future where

"'Every centre of 10,000 people will have it's museum, as England had it's Churches for far and wide in the 13th Century. The churches in the 13th Century were the receptacles of all kinds of art work. Every Church had it's paintings, sculpture, metal decoration, architecture, music and was in fact a museum.'" (9)

Cole saw his museum as a way of doing good, of improving the character of the working man - and thus making him more likely to go to heaven.

"Perhaps the evening opening of Public Museums may furnish a powerful antidote to the gin palace." (10)

Just as God the Father cared for the Israelites, so does the State for its people. Bryan Appleyard recognizes this welfare aspect to state patronage of the Arts, when he notes:

"It is no coincidence, that, to this day, the arts and the health service seem clasped in a bitter embrace when it comes to arguments about money." (11)

5. The Arts Professional

As Vatican Councils, Synods and Assemblies show, it is the passion of involved individuals, the clergy, in desiring to uphold their vision of the true faith, that causes all the trouble. The clergy of Art are of course its professionals; curators, administrators, historians, dealers and critics. For reasons which will become apparent, conservators do not belong to this grouping.

Each of these professionals has a particularly strong link to both Artist and Patron, one elevated above that of the general congregation and involving the exercise of 'taste', as we have seen largely the prerogative of the ruling classes. A 'good eye' with its subtlety of discrimination has a genius of its own almost - but not quite - comparable in mystery to the inspiration of the artist himself.

PART II - CARING FOR OBJECTS

1. Identifying with The Object

I am going now to try to show how serious an Arts Professional's empathy with an object is, and how threatening assaults on this bond by the 'interventions' (a word used repeatedly in the ICOM definition earlier quoted) of a conservator might be.

In her book 'On not being able to paint' Marian Milner quotes Dunoyer de Segonzac:

"For the creation of works of art there is a condition of the spirit that must be achieved and preserved at all costs. This condition can be compared to what the religious term a state of grace. It is a state of exaltation, of communion with life, nature and his fellow beings which enables the artist unconsciously to exalt, re-create and transcribe the world about him." (12)

So to cherish a work of art is to yearn for such a state, or in psychoanalytical terms for a time before we began to suffer the separation of subject and object. For example Peter Fuller describes Ruskin's overwhelming feelings for objects in this way:

"Ruskin's way of handling (and failing to handle) his intimate feelings about separation from, and fusion with the female body - the mother first and potential adult sexual partners later - enthuses and informs his intense responses to the natural world." (13)

When he was 33 Ruskin complained in a letter to his father 'Whatever feelings of attachment I have are to material things' and later 'Pictures are my friends, I have none other'.

In 'A Joy For Ever, the Political Economy of Art' (1851) Ruskin wrote of large public galleries vis a vis restoration

"They are the places of execution of pictures: over their

doors you only want the Dantesque inscription 'Lasciate ogni speranza, voi che entrate.' (14)

The restorer interrupts the secure relationship between Ruskin and pictures, the object is removed for treatment into the first circle of hell; in conservation the connection between loving and destroying is pointedly manifest. To return to Marion Milner:

"What one loves most, because one needs it most, is necessarily separate from oneself; and yet the primitive urge of loving is to make what one loves part of oneself. So that in loving it one has, in one's primitive wish, destroyed it as something separate and outside having an identity of its own." (15)

2. Conservation as intervention

If we see Conservation as public recognition of this urge then we can also see how disturbing it's discipline might be to the Arts Professional. As John Spurling shows here, a use of language which might be more appropriate as the response to a personal insult is frequently employed in the 'defence' of art.

"Who runs the Tate? For a time after Alan Bowness became its director in 1980 it seemed to be the Conservation Department and there were fears that the place would be gradually transformed into a kind of tomb, in which the treasures, deprived of light for their own protection, would become almost invisible to the customers. Several temporary exhibitions were virtually ruined by the Conservation Department's light levels until somebody - presumably Bowness - mastered the brutes, or at least compromised with them and made it possible again for present day visitors to enjoy what was essentially being kept for posterity (though they, of course, wouldn't have been allowed actually to see the treasures either)." (16)

Thus the heroic Arts Professional does battle for his people against the monstrous forces of darkness and death to reclaim the treasures of light, life and the future. In Conservation News 27 Mr Puttock, the administrator of Arundel Castle, puts the conflict between enjoyment and destruction more amiably:

"If I wake up in the morning with the sun streaming through the windows across the bedcovers, I know it is going to be a happy day for me and I also know that is a few years the bedcover will rot and the carpet will fade." (17)

Which is why conservators are **not** ordained members of Art's clergy. Their job is to **intervene** to spoil the fun, to separate subject and object and thence to disrupt the trinity of Arts Professional, Artist and Object. However conservators should be wary of slipping, as they are prone to do, into a puritanical tone of moral reproach in dealing with their clients. News of damage to objects by auction houses, museum officials, builders, the weather, acts of God - anything in fact outside their control provokes a brief ritual song and dance. Eyes cast to the heavens, shoulders shrugging as one hand rests on hip and the other turns palm upwards in despair, they will mutter a chorus of satisfied, resigned song: 'well what can you expect...I told you so...another mechanical error' etc. etc. They are playing with fire, for if they perceived the depth of object/subject bonding in their customers, they would know that to indicate negligence is to risk opening a Pandora's box of negative associations - viz Ruskin, Januszczak and Spurling. And there is something repellent about a profession which depends on decay rather than creation for its existence, though the one is irrevocably part of the other.

3. Cherishing the Past

Undeniably to dwell on the past is to reveal disillusion with the present and distrust of the future. There is a danger that conservationists (the clients of conservators) may over-reach themselves provoking an anti-heritage backlash. Sir Roy Strong expressed the fear that obsession with the past might restrict fostering of contemporary creativity in a letter to The Times in September 1983. Considering the scale of Sir Roy's obligations to conserve the vast collections of the Victoria and Albert Museum which was emphasized by both the Rayner Scrutiny of 1983 (18) and the National Heritage Act 1983 (19) it is no wonder that he was beginning to feel submerged. For the Rayner Scrutiny recommended increased staff and spending on the V & A's Conservation Department, while the National Heritage Act described museums' first duty as to

"Care for, preserve and add to the objects in Museum Collections."

It is important to remember that Conservation is a service industry responding to Arts Professional demand. However Conservation can be used as an emotional dumping ground because its professional existence shows (a) how careless we have been of the past, and (b) how dependent we are on it for our picture of ourselves. The conservator is Art's Dentist. Toothache means I haven't looked after my teeth properly. Pain forces me to go to the dentist who points this out and then hurts me so that inevitable decay is slowed. I hate my dentist because he shows me how I contribute to my own deterioration, and because I need him to relieve me of it's symptoms. It is as unfair for Arts Professionals to berate conservators as it is for me to hate my dentist, knowing which does not make me like him any more.

Of course there are cases, and Morris' famous anti-scrape campaign of the 1870's is one, where such criticism is justified and important, though it is often a rearguard action by Arts Professionals to safeguard that which they hold most dear: their position in the cultural court.

In the blur of sentimental generalized sensation produced by a word like 'heritage', age (patina) has connotations of virtue, and intervention by Scientific Method is an unpalatable as mixing salt with sugar. Perhaps cherishing the past is just a way of escaping the dilemma of modernism, and to discover that jumping from one frying pan is just to land in another fire is an unhappy lesson for conservators to have to teach. Confronting Beckett's picture of contemporary creativity is enough to make any art-speaker look for refuge in the past;

"The expression that there is nothing to express, nothing with which to express, nothing from which to express, no desire to express, together with the obligation to express."
(20)

NOTES

1. International Council of Museums. The Conservator - Restorer: A Definition of the Profession (Copenhagen: ICOM, 1985).
2. Wordsworth in preface to Lyrical Ballads quoted in Raymond Williams Culture and Society (London: Chatto and Windus, 1958).
3. *ibid.*
4. Nicholas Pearson, The State and the Visual Arts (Milton Keynes: the Open University Press, 1982).
5. J M Keynes, The Arts Council: its Policy and Hopes, The Listener 12.7.45 (London: BBC).
6. At a Symposium 'What Price Arts Sponsorship?' (12.6.85) at the Tate Gallery, London.
7. As note 4.
8. *ibid.*
9. Quoted in Henry Cole, Fifty Years of Public Work (London: George Bell and Sons, 1884).
10. *ibid.*
11. Bryan Appleyard, The Culture Club, Crisis in the Arts. (London: Faber and Faber, 1984).
12. Dunoyer de Segonzac as quoted in Marion Milner, On Not Being Able to Paint (London: Heinemann Educational Books, 1950).
13. Peter Fuller, Images of God, the Consolations of Lost Illusions. (London: Chatto and Windus, 1985).
14. *ibid.*
15. Marion Milner. See note 12.
16. John Spurling, Bowness's Bailiwick. The New Statesman 30.5.86 (London, 1986).

17. Conservation News 27 (July 1985) The Client (London: United Kingdom Institute for Conservation, 1985).
18. Rayner Scrutiny (1983) An examination of the administration of the Victoria and Albert Museum.
19. National Heritage Act 1983. 'An Act to establish Boards of Trustees of the Victoria and Albert Museum, the Science Museum, the Armouries and the Royal Botanic Gardens, Kew, to transfer property to them and confer functions on them, to make provision in relation to government grants to, and employment by, armed forces museums, to establish a Historic Buildings and Monuments Commission for England, to confer functions on the Commission, to dissolve the Historic Buildings Council for England and the Ancient Monuments Board for England to amend certain enactments relating to heritage and for connected purposes.'
20. Samuel Beckett, Proust and three dialogues with Georges Duthuit. (London: Calder 1976).

BIBLIOGRAPHY

- International Council for Museums, The Conservator - Restorer: A Definition of the Profession. Copenhagen: ICOM, 1985.
- Williams, Raymond. Culture and Society. London: Chatto and Windus, 1958.
- Pearson, Nicholas. The State and the Visual Arts. (Milton Keynes: the Open University Press, 1982.
- Keynes, J.M., The Arts Council: its Policy and Hopes, The Listener 12.7.45. London: BBC.
- Cole, Henry. Fifty Years of Public Work. London: George Bell and Sons, 1884.
- Appleyard, Bryan. The Culture Club, Crisis in the Arts. London: Faber and Faber, 1984.
- Milner, Marion. On Not Being Able to Paint. London: Heinemann Educational Books, 1950.
- Fuller, Peter. Images of God, the Consolations of Lost Illusions. London: Chatto and Windus, 1985.
- Spurling, John. Bowness's Bailiwick. The New Stateman, 30.5.86. London, 1986.
- Conservation News 27 (July 1985) The Client. London: United Kingdom Institute for Conservation, 1985.
- Beckett, Samuel, Proust and three dialogues with Georges Duthuit. London: Calder, 1976).

PROFESSIONAL ETHICS IN RESTORATION

L.A. Lelekov
All-Union Research Institute of Restoration (VNIIR)
Krestyanskaya pl., 10
Moscow 109172
USSR

The very conception of professional ethics till now remains rather controversial. Many specialists consider ethics in general to be an indivisible single whole. Their opponents start from the famous declaration of F. Engels: "in reality every class and even every profession have the moral of their own" (K. Marx and F. Engels. Works, the 2nd edition, vol. 21, pp. 298-299). Usually it is held, that a professional moral emerges in cases, when as "the object of labour" there occur men in some definite social positions. As an element of common consciousness the professional moral is able to emerge at some different levels. At the lowest of them it contains a random number of purely empirical statements. More rarely it acquires the form of a rigid normative system with strictly defined theoretical principles and respective sanctions. In few words, the professional moral inevitably takes place there where do exist professional relations. In some conflict situations the requirements of professional ethics may contradict mutually. Every field of professional activity strives to solve such contradictions in its own way which circumstance clearly signifies a virtual absence of universal professional ethics, one and same for all trades.

Examinations of ethical problems in the field of restoration are not new, but any notable progress in this direction has not yet been gained. Since 1963 twice there were undertaken attempts to normalize processes of restoration according to rules of ethics, each time by American colleagues from the International Restoration Centre. Also merits a proper attention H. Jedrzejewska's booklet "Ethics in conservation" (Stockholm, 1976). Some separate aspects of ethical kind are periodically viewed in publications on restoration and conservation.

Nonetheless it is easily noticeable that any commonly held international ethical standards are lacking as well as terminology abstract concepts of ethics as far as restoration in general is concerned. Therefore emerges a whole set of interrelated questions, among which as the main one features the next: what can be properly defined as the object of scientific ethics, of course, judging from the point of restoration? If one tries to take for it a practical moral of restorers in accordance with other branches of professional ethics, then an overall situation won't get clearer anyway. A number of moral imperatives in the service of restoration is very small. Besides the central prescription - do not harm the object - any explicit propositions are not numerous. A practical professional moral of the restorers is not yet so ripe and so is not able to produce normative statements, even grossly conventional. H. Jedrzejewska's attempts to supply instead of them purely empirical precepts have not gained much success. But one of her observations appears quite important. Against the common opinion she insists that the whole activity of any restoration specialist consists of a continuously running sequence of interpretations. No facts are given directly in inconditioned perceptions. Presupposed qualities and subtleties of object states all the time are estimated, i.e. interpreted. In other words, ethical questions occur immediately during the first close contact of a restorer with an object before practical intervention, but not only in the process of the latter or after it. But many experts do not bother themselves with this circumstance. The first stages of the process seem to them as relatively free from any aspects of professional ethics. In such an approach there is evident a traditional concept of ethics which reduces it to pondering over consequences of our actions, to an epiphenomenon of any undertakings. But the current period of scientific development urgently demands a respect for prognostics, for a good foreknowledge. A desired result of any important process should be timely planned beforehand, even modelled experimentally, given a necessary scientific and methodical foundation. Underestimations of this important stage of the whole process might be treated as transgressions of professional ethics.

By the way just very aspect almost completely lacks any reflection in the only written code of restoration ethics, which was affirmed in 27th of May 1967. This particular document de-

serves a few words as it characterises the situation in the entire field throughout and certainly would serve as a starting point for examinations of ethical criteria in restoration for some future.

After a short introduction the code exemplifies ethical norms properly. The first one among them declares the necessity for preservation "of aesthetic, historical and physical integrity of an object". Selfevident as it is this declaration seems in no need of any comments. Nonetheless its authors would better explain that crucial moment of restorative practice which emerges from a fundamental opposition between aesthetic and historical integrities of the same object. A demand for an aesthetic integrity imposes upon a restorer desires to fill lacunae anew, to paint them over, to retouch the image and so on. Accordingly a historical integrity is minimized. Under any concrete conditions anywhere the final result of such restorative efforts inescapably will be reduced to compromise, to some loss of aesthetic as well as of historical integrity for a given object. Any universal method or principle for a harmless splicing of both these requirements is absent now, but the code does not reveal this dangerous situation with all necessary clarity. A casual reader may easily think such splicing quite possible.

Thus the principle ground for demonstration of ethical norms in the field of restoration was demarcated in the code poorly. It should be drawn more resolutely and without concealing serious deficiencies.

Among other statements of the code as rather remarkable appears a demand of a single standard for restoration of the objects of different kind and value. It is demand of a single axiological scale or, stating it simpler, of a single moral guiding restorer's actions without comparisons between historical or aesthetic value of two and more respective objects. But in reality almost everywhere two such standards, two kinds of morals, two scales are adopted. Extremely ancient or valuable for our aesthetics art works are treated very cautiously and neatly without interventions into the original image. Their historical integrity is thoroughly respected and warranted to the measure of restorer's possibilities on the level of strict conservation. But later pieces, objects from archaeological or ethnographical collections are often forcibly remade, renewed with a large damage to their historical integrity and authenticity. The degree of their modifications under a restorer's hand can be enormous. The very fact of a stable maintaining of two standards reveals serious imperfections of the modern restoration ethics. So the said position of the code is highly actual, it should be advertised widely and introduced into a current practice. Before that it is necessary, of course, to choose the single desired standard for a constant orientation. Here it is advisable to produce a citation from the code: "regardless of his opinion of its value or quality, the conservator should adhere to the highest and most exacting standard of treatment (II c)".

These straightforward and convincing words which are not liable to false interpretations ought to be taken as the proper base for a choice of moral standards in the field of restoration everywhere.

As it was to be expected, the code argues for the principle of reversibility of materials used by restorers. Herein is implied a possibility of a harmless extraction of new glues and the like from a physical and mechanical structure of an object. But this ideally correct requirement can never be completely realised in practice without some damage to an object. Even the most traditional glues like the egg yolk can not be extracted to the last drop. Therefore this principle remains rather limited in its applicability in practice and in theory. The modern restoration now widely uses irreversible compositions, for example silicons. Their discrimination would mean a real impedance to scientific and technological progress.

Also remarkable are the regulations of the code for public relations of restorers. Theirs consultative and educational roles are heavily stressed. Then restorers must not provide paid expertises, commercial estimations of an object's worth or of process expenditures. They also must not act as market agents. This ethical position is certainly positive and deserves every support.

Up till now the statements of this code seem to be excessively indistinct and overgeneralised in many particularly important

aspects. The current practice can not be properly correlated with them. Nonetheless this code still provides a firm foundation for development of some new and more concrete models of restorative ethics.

Beyond the code considerations there remain many theoretical implications which is quite natural since this document has not pretended to serve any other functions but practical. The first such implication as in every sphere of ethical research deals with a conventionality of ethics in general, of its criteria and applications. Ethics does not exist objectively, its central notions - good and evil - are the results of public agreement as it had been stated by Aristotle and other ancient thinkers. They are products of ideology (nomos) but not of an actual reality (physis) within which an object of restoration efforts resides. This is just the very cause of plurality of moral standards in restoration. So the notions of good and evil in our sphere are necessarily subjective. Therefrom a question arises whether a definite ethical reglamentation of any restorative procedures is possible in general. An affirmative answer can only be construed with a due regard to objectively existing cultural needs irrespectively of the degree of ethical conventionality in question. These cultural needs are expressed in demands for restoration services. Ethics is obliged to provide an optimal fulfilment of such demands with the most minimal damage to cultural inheritance, how it is stated in the above mentioned code. So, if the ethical positions were theoretically wholly conventional, then necessities of their development are stemming from practical activities. Now it is evidently clear that an analysis of this conventionality should be strongly recommended in order to find out in which way it can be applied to practical needs. Any such application would always appear as relative and questionable.

Except that in all preliminary drafts of ethical theories usually remains ignored one very important fact. Not only the foundations of ethics are completely conventional but above that they are partly irrational according to views of F. Nietzsche or A. Camus for that matter. Even our common interpersonal ethics can not be exhausted by rational arguments. This side of the problem has never been studied yet for the field of restoration.

To these deepest overall problems of ethics in general correspond typologically resemblable problems of professional ethics and particularly of restorative one. For example on all three mentioned levels it is equally difficult to discern what precisely ought to be taken for an object of moral estimations. Some experts prefer to take for it labour (actions) irrespectively of its final results. Others think it to be only this very final result, an epiphenomenon. Thirds instead of this move the object of moral estimations from the end of a causal chain to its beginning and declare it to be an aim, a task of actions to be undertaken. Sometimes for such an object they choose even only formal requirements or definitions of related aims or tasks. By definition an object of moral estimation ought to be single and indivisible. Therefore only one among the three discussed positions can appear as correct. Once more we have a chance to stress the conventionality of ethical criteria.

The restorative ethics should influence every stage of a restorer's practical activity but in a real practice it is never so. It's quite enough to search through not numerous publications on our theme and see with all clarity that for ethical problems often are taken additions and overpaintings, renewals of aesthetic effects. About the ethics of consolidation or cleaning there is no almost a single word. But these operations are by far more essential for an object's existence in time.

Next, how ethical is the general terminology of restoration? Restorers themselves, mass media, wider societal circles are fond of the term "regeneration", which literally means the recovery of a complete wholeness of original qualities and characteristics. But such recovery is impossible in principle, it is an illusion. Nobody can prevent the action of physical laws, of molecular disintegration. To our misfortune the real essence of restoration processes consists of something else. Only an outward appearance of an object is regenerated and even that not absolutely. It is achieved by means of alteration of the material substructure. So restoration and regeneration put themselves in synonymity with falsification. Both these terms are liable to be properly called a lie for salvation of our thirst for a historical continuance of culture, a *pia fraus*.

It would be useful to exterminate the term "regeneration" without trace from our professional lexicons though it seems to many the very essence of all professional activities and consequently of professional moral in restoration.

The number such problems is limitless. For example, restoration shares some ethical difficulties with historical sciences, particularly with archaeology. Both these disciplines are to characterise objectively the gone historical reality, precisely identify every its development. But restorers in company with archaeologists still have not defined yet the object of identification. Some of them are eager to take for it cultural and historical functions of ancient art works or utensils whereas others think it to be only related material structures. The last point of view is typical for Italian colleagues. At last thirds declare an aesthetic qualities to be the object of restoration. Such an attitude prevails among Soviet restorers.

In conclusion it is necessary to mention that if the majority of restorative ethics ideologists always correlated its norms with manual operations with current actual processes, the above stated considerations aim at another plane of research, at virtually unknown problem of ethical presuppositions in the minds of restorers, in their professional consciousness.

SUMMARY

The present report deals with comparative analysis of methodological principles underlying artistic science and restoration of art. It is based on the identical nature of the subject studied by these disciplines, and on the unity of their common goal. A correlation has been established between the methods employed in artistic science and restoration. The correlational character of the two methodologies is described in retrospect and with reference to future development.

ARTISTIC EXPERTISE AND RESTORATION

Krasimira Lukicheva
Cand. Hist. Sci.,
All-Union Research Institute of Restoration (VNIIR)
Krestyanskaya pl., 10
Moscow 109172
USSR

The need for comparative analysis of methodological principles underlying artistic science and restoration of art is based on the identical nature of the subject studied by the two disciplines, and on the unity of their ultimate goals. The ultimate goal of the restorative process cannot be approached in isolation from artistic science and other humanitarian subjects which study the material and spiritual cultural heritage. Artistic science is called upon, through cognizance of artistic activity, its immanent laws and specifics, its ties with other domains of society's spiritual life, to amass knowledge on the historical development of consciousness and self-consciousness and to accumulate data on human development in retrospect (which forms the basis for projections into the future), on the essence of the creative capacity and psychology of the human species. These tasks are solved by artistic science through the study of the artistic legacy, an important component of the objectified consciousness of the past epochs.

Restorative interference, which changes the appearance of an art work one way or another, more or less predetermines the scope of knowledge appropriated by artistic science and other humanitarian disciplines. Furthermore, data from the history of restoration, and the investigations of a monument in the process of restoration, can sometimes alter traditional views on the history of art and help re-create the true historical destiny of works of art, and the real interrelation between people and the cultural heritage. This unbreakable bond between restoration and artistic science serves as another reminder of the great responsibility borne by restoration for the destiny of the artistic legacy and points to a rather pressing need for a scientific definition of the goals of the restorative process and the methods that can be used to attain them.

A correlation between the methods used in artistic science and restoration becomes discernible in the course of analysis at the methodological level. A retrospective analysis of these disciplines uncovers a correlation of methods that is often sporadic rather than pre-meditated. But whether or not we realize it, the correlation has existed as long as artistic science and restoration have. Recently, increasingly systematic attempts have been made to carry out objective studies of the interdependence between the methodological principles of both sciences. This should undoubtedly improve the reliability of artistic analysis from the scientific point of view, and help arrive at a clearer definition of the trends and ways leading to scientific foundations for practical restoration.

It seems advantageous to start a comparative analysis of methodological principles followed by artistic science and restoration with expertise due to the following:

- 1) Stylistic analysis, which forms the basis of artistic expertise, has served as the starting point of the scientific history of art. It made it possible to appreciate the work of art as a unique historic, cultural and aesthetic phenomenon, an organic blend of material and spiritual aspects of an individual's creativity. It thereby brought up the issue of the uniqueness and irreproducibility of aesthetic worth and the authenticity of aesthetic information it contains.
- 2) Restorative interference has, and often continues to, distort above all data pertaining to stylistic analysis by adding characteristic touches foreign to the objectively viewed style of the artist, his school, artistic epoch and the specifics of style.
- 3) Expertise and stylistic analysis emerged from the study of painting at a time when restoration matters were solved almost invariably from the strongly predominant positions of the so-called "artistic restoration". These positions in fact boiled down to the falsification of the original to suit the taste of the restorer and the public. In other spheres of restoration, reno-

vation gradually gave way to the method of archaeological restoration with its concept of documentary worth of the monument as a source of objective scientific data. In the sphere of restoration of painting, however, the advent of the scientific approach to the goals and results of the restorative process had for a long time remained blocked with psychologized concepts of aesthetic perception. The concepts that help aesthetic hedonism to be the fundamental platform and the essence of artistic perception also posed a serious obstacle.

This was the brand of psychologism that swept philosophy and the humanitarian sciences; phenomenology as understood by Husserl at the turn of this century, was born in the struggle against psychologism. Phenomenological analysis, however, dealt with problems at the highest - epistemological - level, trying to provide a critical and theoretical definition of the logical foundation and grounds of knowledge per se. There can be no justification in drawing parallels between stylistic analysis and phenomenology: they belong at various levels and are therefore incomparable. Nor would it be correct to look for a cause-and-effect relationship here, since stylistic analysis (cf. J. Morelli) is chronologically slightly ahead of phenomenology. Yet, the formulating principle behind both is one and the same global problem of the epoch - the problem of non-contradictory combination of the objective content of knowledge, and the subjectivity of the process of cognition expressed in the result of the cognitive act. (It should be mentioned, however, that the attempt to leave psychologism out of cognition in general and the interpretation of psychic processes such as perception in particular, could not fail to tell on further humanitarian development. It also influenced artistic analysis, for which the scientific approach to perception processes is of paramount importance).

To solve the above fundamental problem of cognition, the framework of stylistic analysis was used to develop a system which seemed to provide for objective observation of the objective fact. It was based on two preconditions: that a set of hierarchically arranged and formalized characteristics can be used to counter the distorting influence of subjective emotion and the subjectivist attitude of the recipient in the process of analysis of a painting; and that the analyst actually deals with the genuine fact, i.e. the authentic work of art - and not a forgery, copy, or a painting whose artistic structure combines the hand of the author and that of the restorer. It is these preconditions that point to the correlation between methodological principles in artistic science and restoration with special clarity. It was the method of stylistic analysis that has originally shown the need for genuineness of the object of cognition and the data contained therein to be the central condition required for attaining objective cognitive goals in the study of art. This consideration signalled the beginning of a re-orientation in restoration of painting, too.

Artistic expertise is not marked by conceptual unity in the approach to criteria for stylistic analysis. Two trends - the rationalist (or analytical) trend, represented first of all by Italian researchers (Morelli, Cavalcaselle), and the irrationalist (intuitionist) trend, elaborated by German scientists (W. von Bode and M. Friedländer). The method of attribution and expertise of the former is based on analysis of the so-called "secondary stylistic features". They include elements of the painting that have little semantic or artistic import and do not therefore command the viewer's attention. It is believed that the author executes them automatically, without thinking, almost mechanically, which provides for the best illustration of the specifics of his hand. Morelli saw these in the shape of the fingernails, the hand, the fingers, the lower part of the ear and the nostrils, etc. (Further structurization and semantic classification of these features was carried out by Morelli's apprentice, B. Berenson, who used Italian painting for material). Admittedly, analysis of secondary stylistic features yielded substantial results in the correct attribution and determination of the scope of works by a master or a school. Nevertheless, this method is far from being unconditionally correct or universal. But this is not the most important consideration. Restorative interference, as it were, makes this very method inapplicable, since the restorer usually believes that the re-creation of secondary features (which, besides those listed above, may also include background scenery, still life used as an accessory, etc) changes nothing in the artistic image of the painting and can therefore be safely carried out.

The latter trend in artistic expertise upholds intuition and the role of the "first impression" of the expert as criteria of the truth in stylistic analysis. This at once transforms the process of attribution into the sphere of unknown psychic phenomena, which cannot be supported scientifically. The process of cognition, transformed into the irrational sphere, was divided from the results of cognition, which were nevertheless proclaimed scientific and objective. This acted as a source of methodological contradictions which were often difficult to surmount. Such an approach undoubtedly gave off reverberations of psychology, which had been particularly pronounced in German philosophy and the humanitarian sciences that evolved under its impact. Representatives of intuitivist expertise were inconsistent in their views. First, they also resorted to analytical observation of works of art, and, second, they seemed to overlook that intuition and the "first impression" are also based on a prolonged and systematic study or voluminous artistic material.

This trend in the development of expertise is akin to the widespread belief that the restorer is capable of using his intuition to grasp the stylistic specifics of a master, and proceed to re-create the lost parts of the master's work on this basis. It is difficult to say whether this concept in restoration is genetically related to intuitivism in stylistic analysis and attribution. There can be no doubt, however, that the concept of intuitive cognition, of "identifying" with the imagery of the painting propped up this scientifically inconsistent approach, which exists to this day.

The contradiction between the goals of stylistic analysis (objective cognition of a work of art as a unique creation of a unique individual) and the means for attaining these goals (as proposed by the latter trend) is not only theoretical. Its consequences are felt at other levels besides thegnoseological ones. Methodological contradictions in the study of works of art has a direct and negative effect on the methods of their protection and restoration. The contrary is also true: perfected methods of artistic science spur the development of scientific foundations of practical restoration.

While investigating problems related to attribution and expertise, artistic experts paid the closest attention to the role of colour, tone, light-shade modelling, format, scale and composition of the painting in the construction of the artistic image. Dismantling the metaphysical approach to the work of art, they analysed how alteration of these stylistic components during the historical existence of the work, and during the history of its restoration, changed its artistic image and communicated, from the first, a distorting quality to the views on stylistic features and characteristics. This formed the basis for re-thinking the existing concepts on the methods and permissible limits of the restoration process.

The works of artistic experts dedicated to the rules of evolution of the creative individual, the objective signs of authorship and authenticity, and the qualitative and principled difference between a copy and the original, were very important for the theory of restoration as applied to works of art. These data were widely used later to formulate the scientific norms of the process of restoration, the principle of inviolability of the authentic artistic structure of the monument, the principle of maximum preservation of the authentic physical base of the monument as the substance of its artistic qualities, the principle of strict differentiation between the surviving parts of the monument and the restorative interference, and the principle of rejection of re-creation of the lost elements of artistic form. Profound detailed knowledge of a concrete work of art attained with comparative stylistic analysis, provides for a more flexible individual approach to restoration.

The development of physical and physico-chemical methods for restorative investigations of art works stimulated further advance of stylistic analysis per se. Today it is carried out at many levels, having overstepped the boundaries of the visually observed artistic form and into the inner structure of the work where the eye cannot penetrate. Contemporary experts rely on data that characterize the "stratigraphics" of painting (if it is possible to use this term from historical geology here), preparation of priming, application of the primary background, etc. This extends the knowledge on the style of a particular master or school, and the artistic epoch, since the inner structure largely predetermines the qualitative characteristics which we include in the specifics of style.

Mutual influence of restoration and artistic science offers enormous advantages in the future. We are still in the early phase of scientific correlation of their methodologies. It can also develop in the gnoseological aspect. In this sphere, the strict, scientifically correct definition of the basic terms and categories of artistic science, which is still in the future, is bound to produce a favourable effect on the elaboration of the set of notions and categories to be used in theoretical restoration. This is, in fact, only one possible direction for development. Sociological aspects of methodological functioning are no less important. Here, the central issue hinges on the solution of the following contradiction: the art researcher who works at a museum and plans to use stylistic analysis as a means of cognition, attribution of the painting, is bound to formulate the goal of restoration in full compliance with modern scientific requirements. But this same expert, if he is preparing a painting for an exposition, is liable to ask the restorer to violate the original, its authenticity and attain "full" restoration. Argumentation behind such behaviour lies in the sociological sphere; this conflict between gnoseology and sociology seems far from being over.

Summary

PAINT IS NOT PAINTING

Comparison of traditional
techniques for restoration and
characteristics of modern
art.

Dr. Hiltrud Schinzel
art historian and restorer
Bilker Allee 102
D - 4000 Düsseldorf, BRD

I propose to take a closer look at some of the characteristics of modern art - and a glance at the way they might be congruent with some of the familiar characteristics of the restorer's work.

Modern art presents an image of fast pace and constant change, nothing is sure, exemplary or fixed. For the restorer one of the most crucial aspects of modernist ephemerality is its materials - they tend not to be durable - and the mode in which these appear in a work of art. Contemporary art's fleetingness of thought and image leave symptomatic marks in its style. Here we encounter different ideas, genres and techniques side by side, in fusion and in opposition; regarding the genres typical forms are mixed media, environments and installations with traditional genres like graphics, painting and sculpture copulating in merry abandon; regarding technique, the beholder will be prone to equate the cursory or transient with the bad. It is negative only in terms of durability, however, and that, as we have said, is the opposite of modern art's characteristic: transience. If transience is the aim, then the techniques of modern art are entirely adequate. It is this transience that ensures that a work of art, once completed, is already obsolete, the idea no sooner carried out but patinated, the quotation hardly materialised (and how modernists love their quotes) but already viewed with a smile of condescension. This rampant rather than natural growth of ageing-marks, the modernists' 'patina', has nothing venerable or dignified about it. It robs the restorer of the accustomed motivation for activity, namely that shudder of awe at accumulated centuries. The ideological justification of restoration, preservation out of piety, contradicts the transience of modern art (piety towards insurance value is no admissible substitute and piety in the presence of quality presumes a measure of faith in one's ability to judge; the relevance of so-called 'quality' has fallen often enough on the slippery boards of both contemporary taste and forgeries).

The quandary dawns upon us: how to reconcile the stability that is the restorer's goal with the ephemerality of modern art. It makes you think. The art of restoration itself claims the virtue of reversibility, quite in contrast to the static nature of its task of conservation. Ultimately a reversible operation is also ephemeral in concept, like a concert encore that can be given or not, depending on the level of applause, but which is not announced in the printed programme for the work of art. To acknowledge the aims and values of the Moderns forces us to review restoration and its aims and values as we are familiar with them, and thus also the way in which we apply its ideologies and techniques; we should follow this through and look at the first prerequisite for the art of restoration - the work of art.

'The world of the artist is a visible world which is nothing other than visible, an utterly insane world since it is complete and yet only partial,' claims Merleau-Ponty. The point being that art as an entity formed and perceived in purely visual terms can never be comprehended through a non-visual medium. We may understand art with our eyes, but not with words. This is the dilemma of every exercise in art criticism and every theory of restoration. Both art criticism and the declared ideal aims of the restorer smother art with a theoretical construct in a mathematical ideal model. The effort is selfdefeating, since these can satisfy only the laws of the linguistic or semantic model they have set up, but never those of the work of art itself. It is a complete entity as the painter created it in his visual perception of things; and it becomes a new and different entity with each new beholder. The content of the entity as perceived by the artist cannot be identical to the entities perceived by successive beholders, yet the work of art is complete unto itself at each contemplation. In this sense too, the work is never static; the transience typical of modernist work is also typical of the whole genus of visual art. The restorer's striving for immutability in the values of a work of art - the permanence, timelessness and uniqueness which the restorer hopes to guarantee by conservation - is in categorical opposition to what we have just seen to be the essence of the work of art. The ideological roots of restoration today stem from a historical approach whose ideas are non-visual. Restoration with such fundamentally non-visual origins elicits not a visual, but descriptive, documentary and possibly even now, didactic perception

of its subject: it will never be able to take account of the work of art in its entirety - let alone 'bring back' a work of art that has been damaged or destroyed.

The painter - restorer of the Renaissance may not have 'brought back' works of classical antiquity, but he did bring forth a work of art. The restored work was alive for his contemporaries and materialised their ideal notions of a past era. In our case, the laws of historical thinking have entered our flesh and blood. If we as restorers look at a work of art from either an analytical and scientific or a craft - and - material point of view, we will attain a certain descriptive understanding of the materials it is made of, but touch very little on its visual 'content', that is the materials as transmuted into pure vision, into the work of art (of course this knowledge helps us in the treatment of a work of art; but it cannot give us what a visual work of art demands from anyone who hopes to achieve its visual unity.)

As restorers we face the quandary of not being able to be painter since we know that we are not those who created the work in question (and historicism has ensured that we no longer have the necessary positivist naivety); while, precisely because we are not the artist - originator, we will never be able to revitalize the work, for all the forced cautiousness that our job entails. Our one remaining resort is not so much science and its calculate application as more sensibility and visual experience. That is why the most apt restorer will not be the best scientist, any more than the best artisan; today's competent restorer will emerge only from the most practised eyes, the image addict, the visual-freak and visomaniac. For, faced with modern art, the preservation of alien, that is, non-visual values can no longer justify the practice of restoration; what will do so is the right of the work to live and be experienced by the living.

1) Maurice Merleau - Ponty, L'Œil et l'esprit, Éditions Gallimard Paris, 1964

SUMMARY

It may be seen from the materials presented that after all quite a lot has been written on the theory of conservation in Poland and the formulated theses were clearly addressed to practice. The first works referred conservation of architecture and especially to the problems of rebuilding, then to mobile monuments. The subjects considered are concerned with all the most essential problems of conservation such as: individual treatment of works of art, limited and documented restoration of damage, considered intervention in the processes of the destruction of monuments, treating the work of art as a document with the full realization of given conditions, the role of conservation, its range and possibilities and the position of the conservator in executing procedures.

The present paper does not mention all who wrote on the subject of theory of conservation but only the more important authors whose opinions have most influenced conservation practice in Poland.

THEORY OF CONSERVATION IN POLAND AFTER 1945

Władysław Ślesieński
Academy of Fine Arts
Department of Art Conservation
31-108 Kraków, Poland

Contrary to the current conviction in Poland as well, that "in this country problems concerning the theory of conservation are considered extremely rarely and sporadically" the list of more important Polish works in this field since the year 1945 is quite considerable. The article published in 1946 by Jan Zachwatowicz, then chief conservator of the Polish People's Republic, entitled "Programme and Principles of Conservation of Historical Monuments /Program i zasady konserwacji zabytków/ opens it. /Biuletyn Historii Sztuki i Kultury, 1946, 1-2/. The next important papers were "Notes on the Restoration of Historical Monuments" /Uwagi o odbudowie zabytków/ written by Ksawery Piwocki /Biuletyn Historii Sztuki i Kultury, 1946, 3-4/, "Problems of Education in the Field of Conservation of Paintings" /Problemy kształcenia w dziedzinie konserwacji malarstwa/ Ochrona Zabytków, 1948, 2/ by Tadeusz Dobrowolski, "Old and New Art" /Sztuka stara i nowa/ by Józef E. Dutkiewicz /Życie Literackie, 1956, 23/ and "Sentimentalism, Authenticity, Automatism" /Sentymentalizm, autentyczność, automatyzm/ Ochrona Zabytków, 1961, 1-2/ and "The Limits and Necessity of Specialization" /Granice i potrzeba specjalizacji/ Ochrona Zabytków, 1963, 2/ by the same author. Mention should also be made of the work entitled "Discussion on the Principles of Conservation" /Dyskusja o zasadach konserwatorskich/ Ochrona Zabytków, 1966, 2/ by Kazimierz Malinowski and "Problems of the Valuation and Classification of Historical Monuments" /Problemy wartościowania i klasyfikacji zabytków/ Biblioteka Muzealnictwa i Ochrony Zabytków, volume 43, 1976/ as well as articles "Works of Art in Conservation" /Dzieło sztuki w konserwacji/ Tygodnik Powszechny, 1976, 45/ and "Two Aspects of Conservation Proceedings, Collective and Authorial" /Dwa aspekty postępowania konserwatorskiego, zespołowy i autorski/ written by Tadeusz Chrzanowski /Biblioteka Muzealnictwa i Ochrony Zabytków, volume 46, 1976/. The above mentioned articles do not exhaust the list of works on theory of conservation published after the year 1945. But those already quoted show that quite a lot was written.

The second accusation against those concerned with the theory of conservation in Poland was expressed most clearly by Hanna Pieńkowska in the article "Confrontations with Conservation" /Konfrontacje konserwatorskie/ Biuletyn Historii Sztuki, 1970, 1/ as follows: "The lack of interest in the problem of principles and methods of the conservation of historical monuments or may be a disinclination to express views in discussion has undoubtedly become the main cause of extremely varied solutions and trends in conservation existing in Poland beginning with the continuation of the tendency to full reconstruction of destroyed historical monuments, by their purification, forcing them to economic utility, often devastating the real values of a work of art, by endeavours to maintain the authenticity of a work of art - up till efforts in conservation "stage management" linking the historical monument with contemporary art".

In the present paper the author wishes to point out that the activity of many theoreticians has influenced the forming of opinions and methods of contemporary conservation establishing the base of practice. In large degree also contributing to the spreading of aims and principles of the conservation of historical monuments. Obviously all the papers mentioned are reflections of modern social conditions, philosophical and artistic tendencies.

Generally speaking it may be said that development since the beginning of our century has only been modified to an insignificant degree. But they are characterized by less extremity and dogmatism of formulations and by considerable casuality. It may be said that the theory of conservation in Poland is today waiting for a trial of syntetic monographs and codification of scattered thoughts and principles.

In beginning the review of more important formulations in the field of Polish conservation theory it should be stated that in the first years after the Second World War considerations were concentrated around architectural monuments. It was dictated by enormous devastation of these category of monuments during the war and by the necessity to conserve them. The paper by Jan Zachwatowicz /1900-1983/ entitled "The Programme and Principles of the Conservation of Historical Monuments" /1946/ is of fundamental significance in Polish theory. Its theses that "it was necessary to save from the complete ruin the remains of the cultural achievement, at any price, in order that these remains should retain some significance and at least in a certain degree should play the part allotted to historical monuments in the life of the nation and in shaping its culture - it was necessary to give them a form as similar as possible to their proper form... The sense of responsibility to future generations demands the rebuilding of what was ruined, a full and conscious rebuilding... Because monuments are not necessary exclusive to connoisseur but are suggestive documents of history in the service of the masses... Techniques of conservation must be thoroughly scientific, it must make use of all technical and constructional achievements to assure the durability of historical monuments" In spite of that the above theses were not accepted uncritically, which was expressed by Ksawery Piwocki /1901-1974/ in the article "Remarks on Rebuilding..."

"The Programme..." of J. Zachwatowicz gave direction to conservation in Poland in the reconstruction period of the country and abroad is the basis for the definition of certain procedures as "the Polish school of conservation".

In 1948 two articles concerning the theory of conservation of mobile historical monuments were printed, the paper entitled "Problems of Education..." by Tadeusz Dobrowolski /1899-1984/ and "Aesthetics and Ethics in Conservation..." by Bohdan Marconi /1894-1975/. The former contains the following formulation: "It has become a principle to treat each historical monument individually taking into account various circumstances... restricted by certain limits of conservation procedure. These limits are set by the principle of scientific truth in the renovation of a work that is in a work only that which is certainly known to have existed may be reconstructed" /p. 55/. And B. Marconi wrote "we have replaced Rieglow's "do not complete" by the rule "complete as little as possible" /p. 57/... By improving a work of art does not a-

chieve any greater artistic value but unquestionably loses documentary value".

Both mentioned authors are for individual treatment of works of art, for as little reconstruction as possible and only that which is supported by documentary evidence. The above stand point is also supported by Tadeusz Seweryn /1898-1975/ in his paper entitled "Restoration of Ethnographical Exhibits"/kraków, 1949/ when he writes, "Thus if the work of a conservator consists in subtracting or adding of certain parts of physical matter to the picture -theoretically speaking, at the course of centuries, it may result in a work of art repeatedly restored, completely changed materially, ceasing to be authentic and retaining only the name and the title of the work, in its becoming a forgery. As a result of such reasoning it would be a rule...not to interfere in processes of destruction of monuments. It is impossible to preach the principle of passiveness in the face of the transformation of the physical matter of a museum piece. So only the extent of conservation may be controversial and what means ought to be applied to secure museum pieces against destruction"/p.8/. The importance of the three papers quoted in conservation practice is obvious even if the concepts they present have not been realized in full, they are generally accepted.

In the sixties Józef E. Dutkiewicz /1903-1968/ undertook a more extensive attempt at the elaboration of conservation theory problems. He was considered by many as the author of the most controversial theses that is besides the principle of retaining the authenticity of a work of art, the idea of automatism that is the inevitable influence of science and modern art, their ideas and viewpoints on the form of protection of monuments.

The assumptions in his main work "Sentimentalism, Authenticity, Automatism"/1961/ are as follows: "It is not possible to stop disintegration and changes in the works of art entirely. Both the material substance of works of art as well as the conservation of methods and opinions as to the role of old art are subject to destruction and change...In ancient works of art the only values worth preserving are the traces of the authentic creative process and these are to a large degree indestructible. The passing of material forms is a reminder of the necessity of the continual changing of form and taste, of the necessity to mobilize creative forces to supplement the losses and damage caused by the destructive processes of nature. It is characteristic of contemporary culture that it wishes to mark works from foreign periods and places with the appropriate stamp. This ought to be expressed only in the technical means used, which are the expression of domination of our epoch over disorder and disintegration of time...The aesthetic and scientific conservation of monuments of the past just as the scientific principles of their maintenance, are dictated by trends of contemporary trends in art and science...Verification of monuments of the past worthy of conservation, verification of means and ways of conservation follow automatically as a result of formation ideas and viewpoints of new art and also as a result of the development of historical reality and likewise as a result of discovering new emotional values, existing in ancient art. This automatism of consciousness may arise even without the participation or despite the conscious will of man".

Kazimierz Malinowski /1907-1977/ also showed a tendency towards systematic formulation of theoretical opinions in the field of conservation. In his paper entitled "The Discussion on the Principles.." /1966/ K. Malinowski states that: 1. A monumental object is a document of historical events and the culture of a given epoch as well as a testimony of the achievements of a given milieu, 2. As a document it ought to be preserved in unchanged form and be valuable evidence concerning the epoch and the author, 3. The inviolability of a work is a factor of particular importance where works are concerned as they are unrepeated, 4. Destructives are not only evidence but also the substratum of emotions, 5. Certain special considerations of a symbolic nature or resulting from the wish to make them more legible may justify retouching and partial supplementation. Departure from the principles of absolute noninterference may be made only on the basis of a collective decision. Their form and the technique used must be in accordance with contemporary practice up to date and must ensure complete removal and the possibility of differentiating retouches from original parts".

Among contemporary authors concerned with the theory of conservation in Poland mention should be made of Tadeusz Chrzanowski. In his paper entitled "A Work of Art during Conservation" /Tygodnik Powszechny, 1976, 45/ he wrote: "what is the purpose of conservation? Obviously, one of its tasks is to return the object to its original state, that means to remove damages, dirt or later additions, but the main task is to rescue a given art work, to protect its material existence today and as far as possible into the future. Too extensive changes are taking place in the chemical composition in the structure, in workmanship, in the shape itself of the object in general for one to even dream that after the conservation we will have a work of art "as good as new"... New aesthetic qualities appear in place of the old because conservation procedures as such make essential changes in colouring, in workmanship, sometimes even in the structure of the work. Besides that they must reach responsible decisions. They have to find the limit of a procedure, they have to decide of the limits of restoration, they venture certain completely new arrangements. It is a great responsibility as the conservator is not the author of the work...".

The sequel of these ideas are to be found in the next article by this author /1976/ entitled "Two Aspects of Conservation Procedure: The Collective and that of the Author". We read there "...Choosing authorship in conservation may wake a number of reservations. There are basically two causes: firstly, in conservation we are not dealing with the pure creative act, secondly, unfortunately authorship in conservation has been discredited by numerous examples of excess... The so often used and always overused term /or really slogan/ "restoration of a monument to its original state". In reality we may create, by introducing new aesthetic qualities, an impression nearer to the original appearance of a monument, though not identical with it. As a result of this kind of procedure we have the illusion of a certain "original state" which we must after all reconstruct by way of imagination... Today the question of authorship in conservation is not at all clear. It is obscured on one hand by fantasists in the field

of conservation still building their not always scientific visions...and on the other hand by labourers in the field of restoration who treat it as craft and would willingly hide themselves behind the anonymity of their not badly paid occupation. It seems necessary in order to renovate the restorators authority as joint authors of important monuments and works of art and also - for their own good - to limit their field of action by certain restrictions, resulting from their particular, not purely creative but co-creative role...The following are some of the principles 1.absolute respect for the original, 2.concordance with the past, 3.concordance with the assumption of destination /that is with "futurity"/, 4.aesthetic subordination, 5.honest craftsmanship..."



SUMMARY

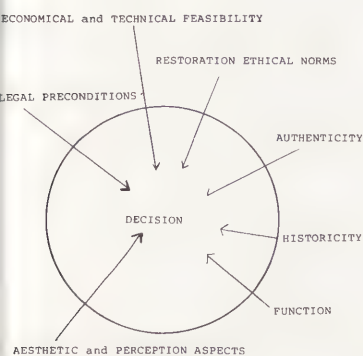
a follow-up of a proposal, launched at the 1984 meeting of ICOM/CC by the coordinator of the working-group "Theory and History of Restoration", a small one-day-symposium was organized at the Central Laboratory in Amsterdam under the title "Interdisciplinary aspects of conservation and restoration".

This meeting was meant to investigate the possibilities for a widening of the interdisciplinary circle concerned with conservation and restoration theoretical problems.

The speakers represent the following disciplines:

Economics, Operations Research, Social Psychology, Museology, Philosophy, Perception Theory, Aesthetics, Art History, Anthropology, Psychoanalysis.

It will be evident from this report that the vistas of the various disciplines may open towards a better understanding of the forces that determine our decisions in conservation and restoration are only hinted at. In one way to deal with ten totally different approaches was attempted much, but the general opinion of the participants at this meeting was that each discipline deserved a much broader and deeper involvement and may then provide most interesting new approaches to areas of concern.



ROAMING THE STAIRS OF THE TOWER OF BABEL

EFFORTS TO EXPAND INTERDISCIPLINARY INVOLVEMENT IN THE THEORY OF RESTORATION

E. van de Wetering & D.H. van Wegen

Central Research Laboratory for Objects of Art and Science

Gabriël Metsustraat 8

1071 EA Amsterdam,

The Netherlands

A proposal for further activities of the working group was launched by the coordinator during the Copenhagen meeting in 1984.

Assuming that in the field of ethics and theory of restoration one tends to become repetitive, it was proposed to stimulate activity in those fields of science and scholarship that border our own. Considering restoration theoretical problems one tends to use arguments from fields in which we all are laymen and one may wonder whether efforts to introduce approaches in this field in a more professional way would benefit to the restoration world. This assumption was the result from designing a model in which a variety of aspects other than the purely technical ones are mapped out. Basically this model boils down to a circle from the orbit of which the vectors of different significant categories point inwards affecting the decision to be taken. The model represents the basic nature of any decision in the field of conservation and restoration as a compromise; a compromise because many of the forces involved are opposed. Any change in our conception and evaluation of the more or less conflicting categories may change the final outcome of the decision. The categories we tend to take into consideration are (1) AUTHENTICITY, which can be subdivided in various forms = the authenticity of the original material, the hypothetical original appearance of the object which is often called the authentic appearance, the subjective experience of authenticity or the aura of authenticity and the authentic function (which will be dealt with under the category function), (2) HISTORICITY, natural ageing traces of use and wear, adaptations in functions or taste, old restorations, maintenance, calamities (with or without historical significance), (3) FUNCTION, original function, present function, (as a source of information, as a demonstration object for educational purpose etc.), (4) AESTHETIC and PERCEPTION ASPECTS, (5) ECONOMICAL and TECHNICAL FEASIBILITY, (6) LEGAL PRECONDITIONS, (7) RESTORATION ETHICAL NORMS, etc.

We tend to use all these concepts rather casually trespassing the borders of disciplines which are not ours, psychology, philosophy, economics, museology, theory of perception, ethics and aesthetics. My proposal then, was to see whether representatives of these disciplines may be stimulated to introduce us to their field and see what they have to offer in order to enable us to deal with their concepts and tools less amateurishly. When trying to rely on the expertise of other disciplines one tends to overestimate the consistency, reliability and objectivity of these disciplines. That is one of the peculiar problems of interdisciplinary work; while aware of the great variety of approaches in one's own discipline one tends to simplify other disciplines as a rather monolithic objective source of information. It always comes as a surprise if not as a disappointment that also they have their different schools and factions and they spend most of the time explaining to us that we are apt to oversimplify their discipline by looking for too simple straightforward answers. None the less, being aware of what is going on in other disciplines may at least prevent us from fooling around too simplistically with outdated or plainly wrong ideas which we ascribe to those fields. They may offer surprising viewpoints or even vistas on our own field from their point of view. Anybody who has ever tried to explain our discipline to representatives of other disciplines must have experienced how amateurishly their ideas are about us. So to involve specialists from other disciplines in our problems means primarily to have them talk about their fields and not about ours and try to manoeuvre to the point where their fields and our field overlap. This is what we have tried to do during a one-day-symposium in the Central Research Laboratory which will be reviewed below and as far as we know was a first exercise of this kind of "wide-angled" interdisciplinary discussion.

Summary of the symposium by D. H. van Wegen

December 17th 1986 a small one-day-symposium was organized in the Central Research Laboratory in Amsterdam under the title "Interdisciplinary aspects of conservation and restoration". This meeting was meant to investigate the possibilities for a widening of the interdisciplinary circle concerned with conservation and restoration problems according to the model explained above.

The range of participants was very wide with the risk of "babylonian confusion". We deliberately chose not to involve representatives of chemistry, physics and the various branches of technology, as that side of the interdisciplinary collaboration already has a long history. The emphasis was on disciplines which were hardly or even never considered relevant although some of the fields like museology and certain branches of philosophy have directly or indirectly been involved before.

The guest speakers were:

- Dr. R. Hueting, economist, specialised in economics on a non profit base, especially in problems of environmental protection working at the Netherlands Central Bureau of Statistics, The Hague.
- Prof. Dr. G. de Leve, professor in operations research, University of Amsterdam.
- Dr. T. Lindeyer, freelance social psychologist.
- Dr. P. van Mensch, who teaches museology at the Reinwardt Academie, the Dutch training institute for museum staff and at Leiden University.
- Dr. G. M. A. Corver, teaching philosophy at Groningen University.
- Dr. J. Walraven, biologist, specialised in visual sensory research, working at TNO (Institute for Perception Research) in Soesterberg.
- Prof. Dr. Paul Philippot, art historian, specialised in theory of restoration, teaching aesthetics at Brussels University.
- Dr. F. Reynders, art historian, specialised in the philosophical aspects in the history of art history, teaching at the University of Amsterdam.
- Prof. Dr. A. A. Gerbrands, anthropologist, specialised in ethno-aesthetics, recently retired from Leiden University.
- Dr. P. G. van de Berg, psychologist and psychoanalyst working in the Valerius Clinic in Amsterdam.

As we aimed only at a first survey of potentialities and problems, we decided not to invite other than Dutch specialists. Apart from Prof. Philippot (who speaks Dutch) all participants were Dutchmen. Three short introductions by insiders in the field of conservation opened the session. Dr. E. van de Wetering from the Central Research Laboratory discussed the particular problems that arise when different disciplines meet on the same subject. Mrs. A. van Grevestein (paintings conservator of the Frans Hals Museum, Haarlem) discussed the mental stresses under which the restorer works as far as they have to do with the decisions to be taken and the responsibilities envisaged. Mr. R. Crèvecoeur sketched the absurdities one comes across when involved in monument care. These short contributions served to introduce the above mentioned specialists as far as necessary into the field of conservation. The invited specialists were expected to introduce the audience, about forty conservators and other insiders, into their field without trying to apply directly to conservation problems. The connection to the conservation field was made during the discussions and questions from the audience. I will touch in short on some of the more promising points that were made during the symposium. As was to be expected, the full potentialities that each discipline may have to offer will have to be sorted out in discussions which go more into length and depth. To be sure, the organisers did not aim at a situation where all these disciplines eventually would become involved directly in discussions concerning restoration projects; we rather hoped to inspire them to do basic research on those aspects of their field that touch at ours.

During the presentation of the ECONOMIST Dr. Hueting one of the questions that are often raised in connection with the costs of restoration and conservation came up: How can one account for the often occurring situation that the costs of treatment considerably surpass the price of the object itself? Hueting saw parallels with the problem as stated in his dissertation New Scarcity and Economic Growth, Amsterdam 1980, in which the question is discussed how many scarce goods can be sacrificed to protect and maintain the natural environment. A simple balance of costs and revenues does not solve the problem as one has to take into account not only benefits for the present, but also the benefits for future generations. An economic model which is able to incorporate these aspects cannot yet be provided, but Hueting demonstrates that the usual calculations taking future benefits into account - up till now carried out on the basis of the interest-rate - provide a wrong image. Just like the natural environment - in particular species of animals and plants - historic and especially art objects are unique, not reproducible once lost, and they belong to everybody. The market price expresses

only part of the value of a work of art. It indicates only the value that one owner at one moment ascribes to the object. But also non-owners attach value to that object, all the more when it is a museum object. By establishing economically sound limits, within which the costs of conservation and restoration measures have to remain, one therefore has also to weigh the benefits from the preservation of cultural property for non-owners and future generations.

OPERATIONS RESEARCH, represented by Prof. De Leve, is the sub-discipline of economics which deals with the description and analysis of the process of taking decisions. Such problems are translated by the operations researcher in mathematical language and solved usually with the help of a computer. Only on the basis of objective criteria the best possible solution is to be reached. The application of operations research usually will be found in the field of management, that is where the elements that constitute the problem can be clearly defined. The less this is the case, like in many restoration projects, the more difficult it is to reach the one optimum decision. To clarify such more complex problems, operations research designs models to map out the problem. Such models facilitate the distinction between essentials and aspects of secondary importance. Collecting and evaluating experience can be used to refine the model. Each decision-situation can be expressed in a model. The utility of a model depends on how concrete its elements represent the situation. The feed-back on the application of the model can help to refine the model.

The degree to which decisions in restoration are determined by the nature of the communication between those involved is difficult to estimate. Social and psychological phenomena affect the discussions often beyond our perception. SOCIAL PSYCHOLOGY as Dr. Lindeyer stated considers each professional field as a language community with its own cognitive horizon. Within such a community there are seemingly self-evident, but hardly ever explicated norms and values. In interdisciplinary communications this can lead to misunderstandings and withdrawal to one's own territory and eventually rigid persistence on one's own point of view. Social psychology analyses the mechanisms in such situations and develops techniques to change and preferably improve communication patterns. It emphasizes that those involved in such interdisciplinary situations should investigate the other's images and explain their points of view in a more elaborate way than common among members of the same language community. Social psychology distinguishes different phases in the process that leads to a decision: (1) motivation, one has to ensure that every member is involved, (2) the definition of the goal and possible sub-goals, (3) the choice of the strategy of the procedure and (4) once a final decision has been reached to review the course of the procedure.

Of essential importance is how to deal with opposition. Overruling a participant early in the discussions may lead to disproportionate obstruction in the end. One of the rules social psychology applies is therefore to start discussions on a broad basis in order to involve participants in the discussion as long as possible.

MUSEOLOGY, dealing with the field of cultural heritage in its entirety, has, according to its representative Dr. Van Mensch, as its most essential concept the object as a carrier of information. Three layers are to be distinguished: (1) The object as material entity, (2) documentation connected with the object and (3) the object's context. Knowledge of the world from which the object originates determines the identity of the object.

While in the world of conservation and restoration there is a growing awareness that the preservation of the material integrity of the object, including the traces of use and time, has the highest priority, museology tends to emphasize more and more the context and function of the object. Here an inevitable friction becomes apparent. Van Mensch voiced the readiness of museologists to sacrifice material authenticity for the benefit of functional authenticity. In the discussion that resulted from this point of view reference was made to Cesare Brandi's basic observation in his *Teoria del restauro*, Rome 1963, that an object is interpreted differently in each period, and that only the material in its preserved state can provide each generation with safe information for an interpretation to be based on. A too radical adaptation of the object to its museal function fixes the object irreversibly to the interpretation at one given moment. After all, the object as

carrier of information contains a great amount of information of which the relevance will only be understood in a nearer or further future. The impression arose from this and former discussions of this topic during the Buenos Aires ICOM conference 1986 that the discipline of museology on one hand and theorists on conservation and restoration on the other hand have to work together closely while developing their concepts. Van Mensch suggested that the ICOM 1989 conference, to be held in Holland, may provide an opportunity to attune the diverging points of view.

The PHILOSOPHER Dr. Corver claimed that the authenticity of an object could be seen as an ethical value. Aesthetic demands may impose cosmetic interventions to increase the readability and enjoyability of the museum object. As for these aesthetic interventions the question arises on which norms they are based. Could aesthetics as a scholarly discipline provide such norms? Corver emphasizes that his discipline is not able to provide a firm methodical basis for decisions on this level. Aesthetics, however, is aiming to analyse the criteria and to establish the conditions under which a consensus can be reached. With the help of semantic models aesthetics can formulate matters of taste with some objectivity.

The relationship between man and museum objects is to a great extent determined by a psycho-physiological process called PERCEPTION. We tend to forget time and again that what we refer to as reality is in fact only what we are able to perceive. Much of what we call restoration in fact boils down to manipulating our perception. Theories of visual perception, Dr. Walraven stated, can help to rationalise the nature of our interventions and the degree to which these interventions can be minimised. Theories of visual perception can also explain certain side-effects of treatment. For instance the well known fact that the removal of yellowed varnish of a painting not only changes the colours and their relationship in the painting, but also has an impact on tonal contrasts and a change of the experience of the third dimension, can be rationalised and therefore controlled to a greater extent by applying certain perception theoretical knowledge.

The complexity of the perception of works of art was the subject of the contribution by Prof. PHILIPPOT, who is well known as one of the foremost theoretists in our field. He stresses the dual awareness; the aesthetic and the historical awareness of the artefact as being in a state of constant tension. In its turn the aesthetic awareness can manifest itself on an intuitive and on a theoretical level. In the past there was little or no uncertainty in the desire to repair the assumed original appearance, as no difference was seen between creating and recreating an artefact. It was mainly in the eighteenth century that the fundamental impossibility of such an endeavour was understood when a work of art was seen as a historical deed in which in principle no intervention is possible without "faking" the object. The restorer is caught in this paradox see e.g. Jürgen Paul "Antikenergänzungen und Ent-Restaurierung, Bericht über die am 13. und 14. Oktober 1971 im Zentralinstitut für Kunstgeschichte abgehaltene Arbeitstagung", *Kunstchronik* 25, 4, 1972, p. 85 - 112. On a theoretical level the aesthetic awareness manifests itself in the "Gestaltung". A work of art only becomes one when it is recognised as such. One is inclined to experience it at the same time as contemporary and as a document that has reached us through the "medium" of Time. Old objects have undergone irreversible changes in the passage through time. The way however a work is experienced by the beholder has equally irreversibly moved away from the original perception of the object in the time and context it originates from. After the period of impressionism for instance it is impossible to experience colour on a fifteenth century object the way it was experienced in the fifteenth century. We also know this alienating effect from the confrontation with foreign cultures. And the past, to use the title of David Lowenthal's book, can be experienced as a foreign country. (David Lowenthal, *The Past is a Foreign Country*, Cambridge 1986.) Objectively, as Philippot stated, the object is there, but in a sense it escapes our perception. The original condition is a theoretical concept. The object is there, but has changed by the mind as well as by Time. The restorer re-establishes a unity that grants the beholder visual access to the object as a "Gestalt", without however committing himself fully to what the actual unity of the object should be, according to its hypothetical original

appearance. Philippot referred to the possibility of perception theory and aesthetics to provide a better understanding of the ways these tasks can be carried out without impairing the original substance of the object.

The ART HISTORIAN Dr. Reynders questions the role of art history itself. Like the museologist Van Mensch he observes a discrepancy between the object and the way it is conceptualised. He however does not aim at bridging this discrepancy. Once we refrain from the idea that objects have to be fitted in a tradition, objects from the past are able to re-inspire the discussion about tradition itself (tradition here meant as our museum culture and our concepts of history usually taken for granted). It is essential to be aware of the relativity of our concept of history and the same can be said of our ideas about the concept of time. An earlier view of history was characterised by the idea that time is finite. For instance for the early Christian culture the year 1000 was such an end of time. An other view of history is a cyclical model (history repeating itself). Our linear concept of time, time without an end, no doubt affects our approach of objects, their past and their future. Reynders here takes a step beyond the position of Philippot in which history is taken as a matter of fact phenomenon, where Reynders' appreciation of the object is much more factual than it is in the case of Philippot.

Alienating either the concept "object" or concepts like "history" or "culture" may have paralysing effects on those who are forced to take decisions about the physical object and its present-day functioning. CULTURAL ANTHROPOLOGY may bring some relief. Prof. Gerbrands, related from his experience as a museum curator and as a researcher in the field of anthropology first emphasized the typical western outlook that manifests itself when a collection of ethnographic objects is organised according to for instance stylistic criteria. On the other hand however, ethno-aesthetic research done by scholars like P. J. Vandenhoutte and Gerbrands himself has shown that in societies, which used to be called primitive such as the Dan in Africa or communities in New Guinea, the appreciation and perception of art objects comes rather close to our own culture. (A. A. Gerbrands, Art as an Element of Culture especially in Negro-Africa, Leiden 1957.) Also the specialist-production and even the existence of connoisseurship as we know it in the West - are common in other cultures.

The position of the restorer towards the object and its creator on one hand and the curator and the museum public on the other is by definition ambivalent if not to say frustrating. The PSYCHOLOGIST and PSYCHO-ANALIST Dr. Van den Berg hinted in his contribution at inner conflicts caused by a traumatising reticence: the unconscious conflict between the restorer and the artist. Compulsive reservedness and scrupulousness in deciding and acting in restoration may be the source of an inner urge towards destruction or other forms of self-manifestation. As members from the audience added, this may result in practical jokes like the well known addition of a bicycle to a sixteenth-century painting, or what is more serious, in an uncontrolled lust for far-reaching reconstructions or other ways for the restorer to express his power over the object.

It will be evident from this report, the vistas the various disciplines may open towards a better understanding of the forces that determine our decisions in conservation and restoration were only hinted at. In one day to deal with ten totally different approaches was a bit much, but the general opinion of the participants of this meeting was that each discipline deserved a much broader and deeper involvement and may then provide most interesting new approaches to areas of concern. If members of ICOM-CC should know of specialists in fields mentioned in this summary or other relevant fields of science and scholarship that may contribute to Theory of Restoration, please contact Dr. E. van de Wetering and D. H. van Wegen, c/o Central Research Laboratory for Objects of Art and Science, Postbus 5132, 1007 AC Amsterdam, The Netherlands.



SUMMARY

This paper deals with museum objects which for certain groups of people still have a religious, ritual or ceremonial significance. This could have consequences for the way such objects are handled and treated by the conservators.

Many ritual objects, especially those from South East Asian, Indian and African cultures, were made according to strict ritual rules that prescribe the use of certain materials and prohibit the use of others. Adhering to these prescriptions renders the object its religious or mystic value; ignoring them would produce a meaningless object.

Often only certain initiated people are allowed to handle or treat ritual objects. Usually, conservators do not qualify as such.

Decay of sacred objects does not necessarily mean a loss of spiritual value. In some cases restoration of such an object can mean an irreversible desecration, while in other cases an object may even require a ritual destruction.

Some religious objects on the other hand, are required to be at least preferred to be as beautiful as possible. Conservation without "cosmetic treatment" would make them unacceptable for devotional practice.

Little attention has up till now been given to such problems. A questionnaire is added to collect information and experiences on this phenomenon.

SOME THEORETICAL CONSIDERATIONS ON THE HANDLING AND CARE OF SACRED OBJECTS IN A MUSEUM CONTEXT

Anneke Weersma

Art historian, University of Utrecht

c/o Central Research Laboratory for Objects of Art and Science

Gabriël Metsustraat 8

1071 EA Amsterdam, The Netherlands

In 1979 the Tropical Museum in Amsterdam designed a new permanent exhibition in its South East Asia department. One part of this exhibition consists of a small temple-like structure, erected to display an altar and several statues of Buddha.

The Dutch Buddhist community, whom regards the Buddha statues as holy images, expressed the wish to keep them in a consecrated room. The Tropical Museum, in agreement with this wish, invited members of the community to perform the necessary ceremonies and thus - one afternoon before the exhibition was opened - 20 Thai monks from a Buddhist monastery in Waalwijk in the Netherlands, came to the museum and consecrated the little temple through prayer and chanting (1).

This incident shows two quite different attitudes towards ritual objects. In museums we tend to interpret these objects exclusively from a scholarly and museological point of view. Originally of course, they were used or intended to be used in religious ceremonies. To the people who made and used the ritual objects, they represent primarily devotional values and sometimes even magical powers. But when they become part of a museum collection, these religious values are substituted by scholarly, educational and aesthetic values and functions. An object of worship in a living religious tradition changes into a document from which we may extract information about that tradition. Moreover, once in a museum, many religious objects are regarded principally as works of art, as typical or rare examples of a certain style, technique, iconography or artist.

There are some museums however, where the ritual function of certain objects is to some extent preserved or even renewed. The example from the Tropical Museum concerned Buddhist objects. The following examples relate to religions other than Buddhism but the same issue is relevant: the objects perform a double role. They are both objects of study in a museum and objects of worship in a living religious tradition. Apart from the first example, these cases also touch on aspects of conservation and restoration.

The Museum of Religious Art in Uden in the Netherlands, preserves devotional and liturgical objects originally belonging to several Catholic communities in the country.

A large part of the collection is not officially owned by the museum but held on loan, and some objects still serve regularly in devotional ceremonies, especially on Catholic festive days. Among them for example is a wooden statue of recumbent Christ, which is returned to the parish church every Easter, to function in its traditional leading part in the Passion-ceremonies (2).

An example from a very different context, and with further reaching consequences, concerns several Canadian anthropological museums. In these museums, the sacred objects purchased from Indians, are made available to the original owners whenever they need them in their rituals. As a result, many ritual "Bundles" for example, are returned regularly to the former owners to be used in ceremonies. From the Indian viewpoint, only certain people are allowed to handle or treat sacred objects. Therefore some of the curators and conservators, for instance of the Provincial Museum of Alberta, have been initiated by the Indians, giving them the ritual right to open and use these "Bundles" when conservation is needed. In Ottawa, Iroquois priests visit the Museum of Man each year to feed the "false face masks", indeed an unexpected conservation method (3)!

Some religious objects require, according to tradition, a ritual death. A statue of a Hindu God in the Ethnological Museum in Berlin (Dahlem) is an example. On the festival day of this God, this statue should have been carried in a procession to the holy river Ganges, to be ritually drowned!

Every time the festival takes place, a new statue is made of clay or papier-mache to ensure its complete dissolution in the water.

A destructive ceremony like this is of course unacceptable for a museum object. As an alternative, some Hindu students living in Berlin have now devised a new ceremony, which does not require the ritual drowning of the God: As an equivalent of the traditional creation of a new statue every year, they repair and repaint the used one and return it to the museum's storerooms, where it

remains out of sight until the following year's ceremony.

Situations like these imply that a museum leaves part of its conservation responsibility to others. Of course, this involves risks and sometimes far-reaching consequences for the material condition of the objects. These consequences however are respected out of respect for the religious traditions of a culture that continues to survive. In fact, the repairs executed by the users are accepted as an authentic addition to the identity of the object.

There is another kind of situation where a similar discrepancy between the original religious approach and the scholarly-museumological approach, is obvious. Here too the objects have a double role that may involve consequences for their conservation. I am referring here, to churches and temples and their furnishings that are still functioning in their traditional devotional context. Many of these have recently been recognized by scholars as important monuments of cultural history. In addition to their original religious value, they have thus acquired a new value and function similar to a museum object.

This paradoxical situation is particularly clear in the account of five German restorers who were commissioned in 1984 to restore the frescoes in two Buddhist temples in Ladakh in North India. The local community, who still uses these temples, did not initiate the restoration. The plans for and financing of the project came from an international organization that intended - mainly influenced by a growing cultural-touristic interest in the area - to preserve the temples from further decay. The frescoes were damaged and barely readable because of dust and soot. Consequently, the artistic quality of the paintings was seriously impaired, that is: from the western and museological point of view of the sponsoring organization. To the people who created the frescoes and still use them in their religious ceremonies, these problems are not at all relevant. According to their Buddhist views, in which the cycle of death and rebirth is essential, religious images do not lose meaning or value as they decay. They represent on a symbolic level "another reality" that remains ever present in the picture, regardless of its material condition. Therefore, the frescoes in the temples of Ladakh are never restored. They are simply left alone or they are newly painted according to ritual methods that preserve their mystical representation value. Only certain priests and monks are permitted to perform this task and they do so in strict adherence to ritual prescriptions of form, colour, working order, materials, techniques, prayers etc. Certain materials for example, should not be used because they are unclean. To ignore these considerations and prescriptions and proceed with the restoration, would have meant a serious desecration of the temples. Out of respect for the people from Ladakh and their religious tradition that is still very much alive, the restorers decided not to treat the frescoes (5).

In Buddhist Ladakh, the gap between the religious and western museological ideas was unbridgeable. Of course not everywhere is the situation completely insoluble. The restoration of the Passion altar-piece in St. John's Cathedral in 's Hertogenbosch in the Netherlands for example, shows that liturgical considerations may influence restoration practice. Since the altar-piece functions as a vital part of the church furnishing, its appearance after treatment was to be acceptable to the parish. Instead of only conserving the original 16th century polychromy and paint, gaps and other irregularities were filled up and retouched to make the images harmonious and better readable, and thus acceptable for liturgical use. Last year, the parish decided to revive the old liturgical tradition of closing the altar wings during Lent. For this reason, the outsides of the wings, which have hitherto only been conserved, will now also be restored to the same standard as the rest of the altar-piece (6).

Summarizing, I hope to have touched on some of the peculiarities concerning ritual objects, that one is likely to encounter when handling or treating them:

- Many ritual objects, especially those from South East Asian, Indian and African cultures, were made according to strict ritual rules that prescribe the use of certain materials and prohibit the use of others. Adhering to these prescriptions renders the object its religious or mystic value; ignoring them would produce a meaningless object (7).
- Often only certain initiated people are allowed to handle or treat ritual objects. Usually, conservators do not qualify as such.

- Decay of the objects does not necessarily mean a loss of spiritual value. In some cases restoration of an object can mean an irreversible desecration, while in other cases an object may even require a ritual destruction.
- Some religious objects on the other hand, are required or at least preferred to be as beautiful as possible. Conservation without "cosmetic treatment" would make them unacceptable for devotional practice.

This summary is of course incomplete and the importance of each aspect varies from case to case. Our museological approach and conservation ideals towards ritual objects, may cause us to overlook these religious considerations. However, an awareness of them is especially relevant if the object that needs treatment is still functioning within a living religious culture.

The following questionnaire is designed to collect information on the use and handling of sacred objects in your museum and your ideas on such issues. Please answer these questions if they apply to your own experiences or those from hearsay (8).

1. Does the collections of your museum contain religious objects originally belonging to a culture that is still to some extent alive?
2. If so, does any of these objects still represent important ritual or religious values to the original owners or their descendants?
3. If so, are these people in any way consulted by your museum about the use, handling and care of sacred objects? For example with respect to:
 - the use of sacred objects in public exhibitions (e. g. limitations on accessibility);
 - special requirements for the people who handle them (e. g. only men are allowed to touch them, initiation of museum personnel, presence of or assistance from a priest while handling them);
 - rituals necessary to maintain the object's spiritual values or powers (e.g. consecration of the room, blessing of the exhibition);
 - conservation methods that do not prejudice the spiritual integrity of sacred objects;
 - other:
 To what extent is your museum actually prepared to meet their wishes? Please describe the cases in some detail.
4. Are any of the objects concerned made available to their original owners or users? And if so, what agreements have been made with respect to the use, preservation, repair and return of the objects?
5. What is your opinion about the cases you just described? For example, do you regard the (re-)use of sacred objects in rituals or ceremonies as a valuable part of their authenticity? Or do you consider the risks involved as unacceptable for museum objects? What, do you think, should be the museum's policy in this respect?

Please send your reply to Dr. E. van de Wetering c/o Central Research Laboratory for Objects of Art and Science, Postbus 5132, 1007 AC Amsterdam, The Netherlands.

References

1. Information given to me in discussion with M.M. Leyten, curator of the Tropical Museum in Amsterdam.
2. Information given to me in discussion with L. van Liebergen, curator of the Museum of Religions Art in Uden.
3. G. Nooter, "Ethics and the acquisition policy of anthropological museums", in Current Anthropology in the Netherlands, ed. by P. Kloos and M.J.M. Claesen, Rotterdam 1987, 156-164. See also S.J. Wolfe and L. Mibach, "Ethical considerations in the conservation of native american sacred objects", Journal of the American Institute for Conservation 23 (1983), no. 1, 1-6. In view of the possible future repatriation of certain Indian objects, the authors suggest to gather information from tribal religious leaders on how sacred objects can be treated without prejudicing their spiritual integrity.

4. Information given to me in discussion with F. Cowan, curator of the Tropical Museum in Amsterdam.
5. H. Portsteffen, Y. Erb and B. Will, "Restauratoren im Himalaya Erfüllungsgelhilfen des Kulturtourismus?", Mitteilungen Deutscher Restauratoren Verband 7 (1985/1986), 76-83.
6. H. E. Mees, W. J. J. Adriaanse en J. van der Vaart, Het lijdensaltaar in de St. Janskathedraal te 's Hertogenbosch, 's Hertogenbosch 1985, 55-71. And some unpublished documents (correspondence) on this restoration from the Rijksdienst Beeldende Kunst in The Hague.
7. M. Kraatz, "Aus der Religionskundlichen Sammlung Marburg; Aussereuropäische Materialien und Techniken an Sammlungsgegenständen aus andern Kulturkreisen", Mitteilungen Deutscher Restauratoren Verband 6 (1984/1985), 34-36. The author gives many examples from different cultures and religions.
8. This questionnaire is based on ideas and draughts from Prof. M.-F. Guedon from University of British Columbia, Vancouver and Dr. E. van de Wetering, Central Research Laboratory, Amsterdam

ON THE APPLICATION OF INDIRECT DATA IN RESTORATION RESEARCH

O.V.Yakhont
All-Union Research Institute of Restoration (VNIIR)
Krestyanskaya pl., 10
Moscow 109172
USSR

L.N.Rastorguev
MIS&S

For a number of years a group of specialists in different fields have been carrying out complex research of the most ancient Russian monumental sculpture - George the Dragonslayer by V.D.Ermolin (XVth century), made of white stone. Its condition, original composition and fragments are being determined and time and cause of significant changes of the sculpture in the past are being revealed.

Different methods, such as petrographic; paleontologic, photographic and others are used to determine fragments and carry out various restoration works.

Besides this basic research, an attempt was made to apply metal analysis in order to date the posts extracted out of different parts of the sculpture.

Differently to dendrology which can date wood rather accurately, it is assumed that in the science of metal it is virtually impossible to date metallic items because the structure of metal depends upon many factors and it is very difficult to trace changes of structure parameters in time. However, with the help of metallography and X-ray analysis one can try to determine the most probable time of metallic item production.

For this purpose one can use the ability of technical metal elements to diffuse into one another even at low atmosphere temperatures at a very low rate. If such ageing continues long enough, it can drastically change a metal structure. That is why due to copper diffusion ancient silver with a high standard of fineness turns yellow on the surface. In iron items made one hundred and more years ago, there are no significant amounts of the second component with traceable diffusion. However, this, in most cases, puddling iron contains considerable amounts of slag inclusions which got there during shingling. That is why it becomes possible to trace, under the microscope, diffusion zones around slag (oxide and phaeolytic) inclusions and determine metal "age" by the width, and sometimes by the colour of these zones. However, the reliability of determining age by the width of an edge around the inclusion, is limited by two factors. First, in order to increase the reliability of such determination, one should have a set of "standard" metallographic specimens with precise metal age dating. Second, it is necessary to have a working and standard material whose surface is free of any corrosion products, because diffusion conditions will change significantly in the presence of thick external scale.

Standard samples, separated in time by one and a half century, were taken from the remnants of original roof edge ornamentation of the Spass-Preobrazhensky Cathedral in Bol'shie Viaz'my and from the remnants of the original roof edge ornamentation of the Ascension church at Kolomenskoye. The remnants of two posts from the body of George and a post from the horse's head of V.D.Ermolin's sculpture were investigated.

Metallographic analysis of etched and unetched metallographic specimens of these posts has shown that a fragment of the post extracted out of the horse's head and one of the two posts of George's right hand are made of quite pure, probably, puddling metal, in which every iron element is framed by slag and oxides, the frame itself being very thin and broken. X-ray microspectrometry of the distribution of elements in the slag inclusion showed no presence of manganese which has been a permanent companion of industrial iron since the middle of the XIXth century till the present time. As the puddling process started in Russia only at the end of the XVIIIth century and thin edging of diffusion products could still be observed, the posts in question could be dated back to the end of the XVIIIth - beginning of the XIXth century. The dating was also supported by the forging technology used when manufacturing faceted pins with a face going neither into metric nor English measures. The second post extracted out

of George's hand, turned out to be a round bar almost with no oxidization. Its diameter went into the inch measure, and the surface of the post showed that the rod had been given a draft through a well manufactured, solid enough and hardly abraded dye. Analysis of the microstructure of the post showed no slag inclusions, with oxides closing frame around the grain, and oxides producing no metal. The X-ray microspectrometry helped reveal the presence of manganese. All these facts prove that this post was made of open-hearth low-carbon steel, and the inch measure of rolling and draft indicates the time of its manufacturing - the end of the XIXth century. We should add that the horse's bridle material is the same as that of the post.

It is necessary to note that different time of manufacturing posts of the equestrian statue of George, determined with the help of metallographic analysis and X-ray microspectrometry, quite coincides with archival data. Posts, dated from the beginning of the XIXth century, correspond to the time when the sculpture was moved from the old pulled down George's church to Michael Malein's cathedral in 1808.

Metal, determined as manufactured at the end of the XIXth century, could appear in certain fragments of the sculpture in the process of wide-scale restoration works carried out in the church, where the sculpture was installed, in 1891.

The same methods helped reveal the origin of two marble busts from the Moscow regional museum, which were to be restored as works of some unknown sculptors in 1983. Metallographic analysis and X-ray microspectrometry of the iron posts, extracted out of these marble pieces, helped determine the time of their manufacture: one of them belonged to the end of the XVIIIth century, the other was made at the very beginning of the XIXth century. The image itself, stylistic analysis and manufacturing techniques were similar to A.M. Golitsyn's sculptural portrait made by Russian sculptor F.E. Shubin (1740-1805). Marble and bronze analogs of this portrait with minor differences can be found in many museums of our country. At the same time it was necessary to find out whether the newly found piece could be a later copy of the portrait. With the help of indirect data, i.e. analysis of the iron post extracted out of the marble bust, it became possible to make sure that it was not an imitation. Similarly, the origin of the other piece, the second marble bust, was determined: a very rare signature of Ya. Semel'hag (1751-1812), a Swedish sculptor, who worked in Russia for many years, was discovered in it during restoration. A number of technical and documental data backed the assumption that the second bust was made by the famous sculptor during his work with F.E. Shubin.

Sometimes, when analysing metal, it becomes possible to solve the problem without turning to standards, in case the metal belongs to the XIXth century. Thus, it became possible to date the brass frame of A.S. Pushkin's deathmask on the basis of differences between the chemical composition of the deathmask brass and modern types and characteristics of the latter, which appeared in Russia after the Crimean war (1853-1856). Stylistic analysis of the literature and archival data helped relate the mask to the name of Palazzi, a sculptor and moulder who worked in Russia in the 30-50s of the XIXth century. Metallographic analysis has shown that metal contains almost no oxides and slags, and there is no diffusion "edging" of inclusions. Metal purity indicates crucible process, absence of "edging" - the XIXth century, and uneven broaching - the fact that it was made by hand which left certain traces on the wire surface. All the abovementioned data prove that this brass wire was manufactured before the Crimean war, i.e. when sculptor Palazzi worked in Russia.

In conclusion we would like to cite the words of Academician D.S. Likhachev who well understands the importance of indirect data when determining the origin of old pieces of art: "It often happens that minor information turns out to be of paramount importance in case of attribution, and paramount information becomes minor".

principales méthodes de conservation des monuments exposés en plein air font l'objet du présent rapport. On fournit quelques données sur l'utilisation des copies dans l'histoire de l'art, dans la restauration, on cite des exemples relatifs à l'utilisation de copies sur des travaux de conservation antiques.

O.V. Yakhont
Institut de Recherches Scientifiques pour La Restauration
au niveau de l'Union (VNIIR)
Krestyanskaya pl., 10
Moscou 109172
URSS

On n'ignore pas qu'actuellement le nombre de monuments nécessitant une conservation urgente ou une restauration augmente en progression géométrique. Une des causes principales de ce phénomène consiste en ce que l'ambiance écologique s'est vue empirer au milieu de notre siècle d'où une détérioration rapide de matériaux utilisés pour la création des oeuvres d'art et d'architecture. Vu la résistance insuffisante aux nouvelles charges écologiques des matériaux traditionnels tels que l'albâtre, le gypse, le marbre etc., on ne peut pas les utiliser largement, comme auparavant, en plein air dans les villes modernes. A noter que même des matériaux plus résistants, comme le granit, traités par certaines méthodes traditionnelles ne supportent pas non plus des charges contemporaines du milieu agressif. C'est pourquoi, pour assurer la stabilité de sculptures et de pièces d'architecture exposées en plein air, leurs surfaces doivent être bien consolidées: meulées ou bien, ce qui est mieux, polies. C'est bien dommage que jusqu'à maintenant on ne puisse pas se détacher souvent des traditions esthétiques, technologiques, économiques ou par simple inertie on continue à choisir les matériaux d'une manière traditionnelle et reste fidèle à la technique habituelle lors de la création des oeuvres d'art. On peut voir la même chose dans le domaine de conservation et de restauration où l'on garde souvent la vision traditionnelle des mesures et des décisions à prendre. Il s'ensuit qu'au nombre important des monuments de l'art qu'on doit sauver on en ajoute de nouveaux: parmi ces monuments on voit des monuments anciens révélés récemment lors des fouilles archéologiques multiples de nos jours, des monuments qui n'ont pas attiré notre attention auparavant, on y voit aussi de nouvelles oeuvres d'art et d'architecture contemporaines qu'on crée actuellement en matériaux et techniques traditionnels. Malheureusement ce nombre est encore reconstitué par des oeuvres qui ont été soumises, aujourd'hui ou avant, à un traitement de conservation ou de restauration erroné. Il en découle qu'il est actuellement très important de choisir correctement les formes des travaux de conservation pour assurer la stabilité de l'état de conservation des oeuvres d'art au moins pour notre siècle et pour le siècle à venir avant qu'on ne résolve à l'échelle internationale le problème de rétablissement du milieu écologique inoffensif.

A notre avis il existe trois moyens qui permettront de conserver des monuments se trouvant en plein air. Cela concerne des sculptures faisant partie de divers monuments architecturaux aussi bien que des sculptures proprement dites.

Moyen 1. Il prévoit la fabrication de revêtements spéciaux transparents qui peuvent isoler complètement ou partiellement un monument ou ses pièces en les mettant hors de contact direct avec des facteurs les plus nocifs du milieu ambiant. Ce sont des auvents d'appoint sur des bâtiments au-dessus des pièces à conserver ou des housses transparentes de verres organiques, des pavillons pourvus d'orifices spéciaux qui assurent une ventilation naturelle mais interdisent la pénétration de jets directs de pluie et de neige. Un tel revêtement de verre transparent a été fait, il y a déjà six ans, sur le monument funéraire de N.S. Allilouïeva au cimetière du monastère Novodévitchi à Moscou. Son utilisation a non seulement arrêté la détérioration de la surface de la sculpture de marbre due à la neige, à la glace et aux pluies, mais grâce aux orifices pratiques dans celui-ci qu'on a bien calculés et disposés par rapport à la surface de la terre et grâce à sa disposition sur le monument, ledit revêtement a préservé le monument des biodétériorations par lesquelles ont été atteints des monuments voisins l'année passée. Un tel revêtement n'empêche pas de percevoir une oeuvre d'art mais rend plus stable son état de conservation. Parfois les collaborateurs de musée ont peur de créer des constructions modernes supplémentaires troublant la perception habituelle d'un monument. Il nous semble que dans les cas extrêmes (l'exécution des travaux de conservation et de restauration ne se fait que dans lesdits cas) le moyen proposé est moins dangereux pour une oeuvre d'art car il ne conduit pas à une intervention directe dans le monument. Quant à la qualité d'un matériau utilisé pour ledit revêtement, il faut qu'il soit résistant au milieu agressif d'un endroit donné tandis que la forme de revêtement doit être une forme individuelle qui ne défigure pas le monument.

Moyen 2. Ce mode de prolongation de la vie des sculptures de pierre exposées en plein air consiste aujourd'hui en imprégnation partielle de la surface d'un monument ou de ses fragments. Pour l'imprégnation on utilise des produits organo-siliciés et des vernis. Il y a une vingtaine d'années qu'on effectue de pareils travaux sur l'ensemble de sculptures de parc du musée d'Arkhangelskoe. Tous les cinq ans on fait le nettoyage périodique en libérant les monuments des biodétériorations en se servant d'un produit Katamine B pour les couvrir après d'un vernis organo-silicié MCH-7 (en toluène de 2 à 8%). A présent dans le monde entier on utilise beaucoup de nouveaux matériaux brevetés, parfois on utilise des matériaux anciens dont l'emploi tantôt est refusé, tantôt est accepté de nouveau. Il n'est pas rare que l'utilisation de ces derniers soit bien motivée, voire indispensable, mais il y a des cas où leur utilisation est à débattre

et peut conduire à des conséquences malheureuses. Dans ce cas-là, il faut que chaque matériau de conservation soit contrôlé pendant plusieurs années sur des pierres concrètes, dans des conditions concrètes et dans un état concret. Il faut qu'on suive une discipline technologique draconienne, on ne doit pas compter sur des effets inattendus. De plus, il est important de voir les problèmes dans leur ensemble, dans un milieu écologique concret en supposant ce milieu plus agressif qu'on ne le croyait par tradition. Il est probable qu'on aura succès là où on ne considère pas des problèmes à résoudre comme un travail à chaîne, mais comme un travail avec un monument isolé avec des exigences concrètes. Bien qu'à la première vue cette manière d'aborder le sujet nous semble coûteuse et exige beaucoup de main d'oeuvre, la qualité et la longévité de ce qu'on fera déterminera la rentabilité de cette attitude (c'est beaucoup mieux de faire ainsi que de corriger les fautes après ou bien de perdre pratiquement le monument proprement dit). L'intensification et l'industrialisation des travaux de conservation de nos jours auxquels tendent tant les restaurateurs et les conservateurs doivent être dans le domaine d'approvisionnement en matériau de conservation de bonne qualité et de destination multiple, en équipements qui facilitent leur travail, elles doivent se manifester dans une large utilisation des résultats d'investigations multiples, dans l'engagement des calculateurs électroniques lors des recherches de solutions etc.

Moyen 3. Ce procédé de conservation d'un monument unique (ou de son fragment) exposé en plein air consiste à substituer l'original, qu'on transfère à l'intérieur d'un musée, à sa copie ou à son moulage. L'histoire de fabrication de copies tirées de chefs-d'art prend ses racines dans l'antiquité. A l'époque de l'hellénisme on faisait beaucoup de copies tirées de sculptures remarquables et on les transportait aux colonies. Pas mal de sculpteurs s'étaient rendus célèbres par leur métier de faire les copies. Quant aux copies elles-mêmes, on les considérait à cette époque-là comme équivalents idéologiques et plastiques des originaux connus. Les savants de nos jours affirment que ces copies représentent dans une certaine mesure une interprétation créatrice des originaux connus (on faisait souvent des copies de marbre en les tirant des originaux en bronze). De plus, grâce aux copies bien conservées, les historiens de l'art ont réussi à reconstruire le principal canevas de l'évolution de l'art de la sculpture de la Grèce antique et de la Rome ancienne.

Depuis la Renaissance et jusqu'au début de notre siècle, la fabrication de copies et de moulages ne poursuivait que deux buts: d'une part, pour les études (enseignement et formation des peintres), et d'autre part cela permettait à un modeste collectionneur d'avoir, dans une certaine mesure, un analogue artistique (reproduction tridimensionnelle) d'une sculpture célèbre. A la fin du XIX-ième et au début de notre siècle les moulages servaient de matériau scientifique-méthodique: on les utilisait pour réviser et reconstruire les formes et les compositions d'anciennes sculptures (activités de Klein à Prague). Les tâches scientifiques et civilisatrices de cette période ont stimulé, dans une certaine mesure, la création des musées de moulages à Moscou, Prague, Pittsburgh etc. En même temps, on voit naître la pratique de substitution de l'original sa copie ("David" par Michel-Ange à Florence).

Malheureusement, vers le deuxième quart du XX-ième siècle, et surtout après la Deuxième Guerre Mondiale il arrive une certaine variation dans l'appréciation d'anciens monuments: les positions scientifiques et esthétiques cèdent leur place à un point de vue commercial (comme dépôt avantageux de capitaux). Depuis lors on ne s'intéresse pas aux moulages (même aux moulages parfaits tirés des oeuvres remarquables), seules quelques institutions des arts plastiques gardent encore leur intérêt aux moulages. Les anciens musées de moulages disparaissent rapidement. On voit apparaître à leur place des expositions ne comportant que des oeuvres originales (on y voyait souvent des choses occasionnelles, grand regret une telle réorganisation a privé la culture contemporaine d'étonnantes collections systématisées d'une grande importance scientifique et esthétique. Vu que le niveau de fabrication de moulages à la fin du dernier et au début de notre siècle a vu un extraordinaire essor qualificatif et que le choix systématique des moulages a permis de créer dans toute une série de centres culturels des collections uniques qui fixaient d'une manière documentaire l'état de divers monuments célèbres, en provenance de plusieurs coins du globe, dans une période déterminée de leur vie (la fabrication date de la fin du XIX-ième siècle), la perte de ces documents tridimensionnels s'est avérée comme une perte irréparable. Cela s'accroît encore par le fait que certains monuments anciens durant la Deuxième Guerre Mondiale ont été définitivement détruits ou fort endommagés. Certaines sculptures ont subi durant les dernières décennies des travaux relatifs à l'enlèvement d'intégrations tardives et à des réfections parfois injustifiées. Ainsi une couche unique de la culture des siècles écoulés (copies et moulages) se trouve perdue dans une grande mesure, ce qui est dû à la sous-estimation contemporaine. Ce n'est pas tout! Les anciennes techniques unique de leur fabrication, on les a oubliées.

Une altération générale du milieu écologique nous oblige de faire renaître cette activité technico-artistique. A cet égard des problèmes paradoxaux inattendus se font voir: problèmes de tirage des copies et de prise des moulages à partir des copies et moulages du XVII-ième siècle ou du XIX-ième siècle tirés jadis des sculptures célèbres. Lesdites copies ont vu quelques modifications non seule-

ment pendant leur fabrication mais aussi bien durant les années écoulées. Maintenant ce sont des monuments individuels d'un ensemble concret qui présentent une valeur historique et artistique de musée. C'est pourquoi le problème de leur conservation ou de substitution se pose d'une manière particulière et exige une résolution individuelle (on doit les sauver, ces monuments).

Quant à nos jours, il faut noter que la substitution d'un original à une copie à partir d'un même matériau s'est montrée inefficace dans plusieurs cas. Les copies des compositions de I. Vitali (milieu du XIX-ième siècle) de la porte de la Maison d'Éducation de Moscou faites à la fin des années 1960 à partir de la même pierre blanche (calcaire) ont commencé à se détériorer après quelques années et ont déjà subi quelques restaurations. Maintenant leur état de conservation ne diffère pas de celui des originaux qui avaient été faits il y a un siècle et demi. Il en découle qu'en faisant le choix d'un matériau pour la fabrication des copies il faut se laisser guider par les conditions d'agressivité d'un milieu écologique donné et non par les notions traditionnelles.

Il est possible qu'il serait plus efficace de prendre les moulages en utilisant des matériaux contemporains plus résistants, par exemple tels que les ciments polymérisés avec revêtement spécial ou les acrylates cyaniques.¹ A propos, actuellement la prise de moulages est beaucoup plus simple et moins chère que la taille des copies d'après la technique traditionnelle à partir d'un matériau aussi traditionnel. La simplicité de fabrication des moulages s'explique tout d'abord par l'apparition dans la restauration d'un grand nombre de caoutchoucs artificiels se durcissant à froid et de divers matériaux synthétiques. Certes, on fera une erreur si l'on néglige l'expérience ancienne, la technique traditionnelle, car cet arsenal multiséculaire comporte pas mal de techniques simples et optimales. A titre d'exemple on peut prendre le problème de graissage de la surface de sculpture lors du formage. Parfois on utilise des graisses et vernis modernes qui pénètrent dans les pores de pierre d'un original d'où on ne peut pratiquement pas les extraire ce qui détériore le monument. Cependant, il existe un moyen simple qui prévoit l'utilisation de la mousse de savon pour enfants (savon mou) pour recouvrir la surface d'une sculpture de pierre. Ledit savon est absolument inoffensif pour la pierre et protège bien le monument contre l'adhésion d'un matériau de moulage. La surface atteinte d'une sculpture peut être protégée en appliquant soigneusement des feuilles de papier pelure mouillées servant d'une couche de séparation lors de la prise des moulages.

Dans certains cas quand un original est partiellement ou complètement perdu on peut recourir, en vue de restitution d'une sculpture ou d'un ensemble architectural, à la création d'une maquette-copie en se servant des méthodes stéréogramétriques (en cas de présence de photos d'archives) comme on l'a fait lors de la restauration de la sculpture de Saint Georges combattant le Dragon (XV-ième siècle) du Kremlin de Moscou.²

Pour conclure il faut noter que lorsqu'on recourt à une substitution d'une pièce originale endommagée à une copie, l'exécutant doit conserver cette pièce originale et la remettre à un musée ou bien à un dépôt respectif. On peut citer beaucoup d'exemples relatifs à la restauration architecturale où l'exécutant ne s'intéresse aux dites pièces qu'au point de vue de leur utilité à titre de modèle pour en tirer une copie, puis il n'y s'intéresse point et on les perd. Mais ces pièces-là, ne sont-elles pas une partie importante de la culture du passé?

Il reste encore un point à noter. D'une part les buts d'exposition de musée et la nécessité de meilleures conditions pour la conservation de monuments nous poussent à retirer un monument tout entier et non une partie isolée ou un fragment quelconque d'une statue ou d'un relief, mais d'autre part une ajouture insignifiante ne défigurera pas les pièces bien conservées d'une sculpture donnée (on fera sa copie et on la remplacera toute entière). Il faut bien retenir qu'il vaut mieux entretenir régulièrement les objets d'art que de dépenser plus tard des forces et moyens énormes pour leur restitution.

Bibliographie

1. Yakhont, Oleg. "On the restoration methods of museum stone sculpture." Second International restorer seminar, Budapest, 1979, p. 87-94.
2. Museus, L., Yakhont, O., Okunkov, V., Kalantarov, E. "Complex scientific examination on the 15th century St. George sculpture from the Moscow Kremlin." ICOM Committee for Conservation the triennial Meeting. Copenhagen, 1984 (84.1.32).



SUMMARY

The article discusses the activity of the Institute of Archaeological Technology (1919-1937). The Institute, attached to the State Academy of History of Material Culture, was the first establishment in the Soviet Union to take up the problems of restoration and conservation of both archaeological finds and museum articles of artistic value. The Institute relied on many outstanding Russian scholars: Academician of mineralogy E. Fersman, historian and art critic M. V. Fermakovsky, chemist and art critic A. Schavinsky, art critic I. Dmitriev, and others.

THE FIRST RESEARCH INSTITUTE FOR RESTORATION AND CONSERVATION OF ARCHAEOLOGICAL FINDS IN THE USSR

N. N. Zhukova
All-Union Research Institute of Restoration (VNIIR)
Krestyanskaya pl., 10
Moscow 109172
USSR

After the triumph of the October Revolution, the Soviet State started to create a national system for the preservation and restoration of historical and cultural monuments. In order to preserve the invaluable treasures of our culture, both in museums and at archaeological sites, scientists and restorers had to concentrate their joint efforts to define the conditions required to prevent them from decay and destruction. For this end, the Institute of Archaeological Technology (IAT) was founded under the aegis of the (Russian) State Academy of History of Material Culture in October, 1919, to study and preserve museum articles of artistic value and archaeological finds. No country in the world had a similar establishment at the time.

At different periods of time during the Institute's existence (1919-1937), it employed the services of such outstanding scientists as M. V. Farmakovsky (chemist, art critic and historian), V. A. Schavinsky* (chemist and art critic), I. A. Galnbek (metallist), V. N. Kononov (chemist specializing in restoration of fabrics), P. I. Dmitriev (restorer of frescoes), and others. Since October, 1920, the Institute was headed by Academician A. E. Fersman**. The Institute had 5 departments (stone, pottery and glass, technology of paints and painting technique, metals, organic remnants), designed in accordance with the character and objects of mainline research.

In 1919-1920, the Institute's staff headed by A. E. Fersman carried out large-scale investigations in order to attribute and document collections of semiprecious and precious stones in the Kremlin's Almazny Fund, the Hermitage and the Museum of Fine Arts in Moscow. They tested cleaning and storage methods for museum articles, developed a composition for marble cleaning and studied mineral polishing methods. A large collection of semiprecious stones later became the basis for the Institute's museum. At the time, A. E. Fersman published his works, "Tasks of Analysis" and "Precious and Coloured Stones of Russia".

The workers of the Institute's Department of Stone solved the problem of crumbling marble in the halls of the new buildings of the Russian Museum. This work was carried out by the Institute's specialists V. A. Schavinsky and A. T. Fedotov and Professors N. A. Zamyatchensky and A. A. Baikov, chemists who were invited to take part in the project. It was proved that the main hazard to marble lay in mortar grouts used in construction. The specialists did not confine themselves to establishing the destructive role of mortar; they also compiled relevant recommendations for construction workers.

* V. A. Schavinsky (1868-1924) - a professional chemical engineer (graduate from the Zurich Polytechnic) and expert in the history of painting. He collected numerous materials on the history of paints and painting technique in Russia from ancient times (he investigated over 50 ancient manuscripts, notes of foreign visitors to Russia, Acts of the Moscow Armory Chamber, Byzantine literature on alchemy, and other sources). His main work, "Essays on the History of Painting Technique and Paint Technology in Ancient Rus" was published in 1935 (Izvestia GAIMK, 115).

** A. E. Fersman (1883-1945) - the Soviet Union's foremost authority on mineralogy and geochemistry. Academician. In 1907-1909, he worked in the Paris laboratory of mineralogist and petrographist A. Lacroix and in the Heidelberg laboratory of V. Goldschmidt, the crystallographist who co-authored the work on diamonds with Fersman in 1911.

A. E. Fersman analyzed mineral deposits on the territory of the USSR, Sweden, Norway, Denmark, Italy, Germany, Czechoslovakia, Switzerland and Belgium.

His main works include "Precious and Coloured Stones of Russia", vol. 1-2, Petrograd-Leningrad, 1920-1925; "Colours of Minerals", Moscow, 1936.

One of the central problems that occupied the attention of the Department of Painting Technique and Paint Technology headed by A.V.Schavinsky had been various aspects of conservation and restoration of pieces of ancient Russian painting. Numerous works of art were lost in clumsy and incompetent restoration carried out by both solitary artisans and whole restoration workshops. Extensive research covered the entire range of means used in restoration, testing via chemical analysis and physico-mathematical experiments. In December, 1919, V.A.Schavinsky was invited as an expert to serve on the state committee that investigated the causes of damage to the frescoes of the Spaso-Meredit'skaya Church (12th century) near Novgorod. This became one of the first attempts at joint work by archaeologists, architects, geologists, restorers, artists and chemists. A.V.Schavinsky formulated a theory according to which the blame for the disruption of natural ventilation of the church was placed with cement lining, which had been installed during the latest redecoration. Analysis of plaster and painting fragments carried out in the laboratories of the Institute served to confirm the suspicions of the scientist. Participation of the Institute's associates in the work of the committee promoted the prestige of the young scientific establishment. The department also studied the ancient folk methods of manufacture for consumer goods such as dyes for fabrics and yarn. In 1923, V.A.Schavinsky published an article on this subject called "Live Archaeology and New Forms" in the "Kraevedenie" journal.

One of the founders, managers and foremost experts of the Institute, M.V.Farmakovskiy*, first headed the Department of Pottery and Glass, and later - the Laboratory for Research, Conservation and Restoration of ancient fabrics found by the P.K.Kozlov Mongolo-Tibet Expedition, which he helped found in 1924-25. He also presided over investigations of vitreous maladies, which had been very important for museum storage. Fight types of vitreous destruction had been singled out, together with the reasons behind these processes. Unfortunately, scientists did not yet possess data which could be used for putting together recommendations to avoid glass destruction. Experiments were mounted to check the previously used methods of glass restoration. A large-scale study of decorative Turkistan ceramics was carried out. The ancient technology for ceramic tile production was re-discovered.

The Department of Metal, headed by I.A.Galnbek, studied a malady of tin ware known as "tin plague". At the time, the problem was vital to all museums. Experts from the Institute of Physico-chemical analysis of the USSR Academy of Sciences, headed by Academician N.S.Kurnakov, took part in this project. The method for treating "tin plague" devised at the Institute had been successfully applied in the Russian Museum. Instructions on "tin treatment" were compiled, printed and disseminated. I.A.Galnbek published an article entitled "Tin in Our Museums and its Storage" in the "Argonavty" journal (No 1, 1923). He also prepared a 6-volume work under the title "Tin and Tin Deposits in Russia". In accordance with the request of the Russian Museum, his department also analyzed the causes and nature of white filmy deposits on silverware that appeared in moist, unheated rooms.

The Department of Organic Remnants headed by Prof. M.I.Tikhov, investigated and distributed bone materials from archaeological sites in Olvia (the Crimea) and Staraya Ladoga (near Leningrad).

In the period from 1924 to 1931, the Institute of Archaeological Technology published 12 issues of "Materials on the Methodology of Archaeological Technology" in the spheres of organic materials, metals, fabric and ceramic restoration. The issues dealt with the creation of a scientific platform for restoration and conservation. They related news of foreign publications on restoration and preservation of artistic works and ancient pieces, and described the latest conservation methods used in Europe and the Soviet Union at that time. Paying a great deal of attention to restoration and conservation, the staff workers of the Institute believed that "restoration of museum articles is

* M.V.Farmakovskiy (1873-1946) - an acclaimed expert of museum storage and restoration. In 1895 he graduated from the Novorossiysk University in Odessa, and in 1902 - from the Dusseldorf Academy of Fine Arts (painting). He was awarded the title of Doctor of Historical Sciences after his work, "Methods for Studying Ancient Fabrics" came out in 1946. His work, "Conservation and Restoration of Museum Collections" is still valuable today (published in Leningrad in 1947).

essentially an organic element of active conservation. Articles must be conserved not only for a short term, but with a guaranteed prolonged existence"¹⁾).

In the sphere of restoration, the Institute worked together with the Hermitage, the Russian Museum, the State Historical Museum and the Tretyakov Gallery. As the Institute's reputation in matters of restoration and conservation grew, museums from all over the country sought consultations with Institute workers in practical problems more and more often.

The work performed by the Institute was displayed at an exhibition in 1928. The exhibition showed the consistent improvement of analytical methods, the use of methods from natural sciences for restoration and investigation of archaeological and museum objects, together with examples of their implementation in practical work at the Institute. A special place was allotted to photoanalysis of archaeological objects used in photodocumenting, determination of hues and colours.

This was the first successful experience in the sphere of restoration exhibits, which served to illustrate both the "finished products" and the so-called "restorer's kitchen", the process of restoration and the course of preliminary scientific investigations.

In the 30s, the tasks faced by the Institute were aggravated by repeated reorganizations. In 1931-1937, it was called the Institute of Historical Technology (IHT), with two departments: the Department of Historical Technology and the Department of Restoration and Conservation, headed by V.V. Danilevsky and M.V. Farmakovsky, respectively.

At the time, IHT carried out restoration work on M.V. Lomonosov's mosaic panel, "Poltavskaya batalia" ("The Battle of Poltava") (1764). The works on mosaic started in 1925, had to be postponed due to lack of experience and materials. In 1931, when a "green box" had been found at the Mineralogical Museum of the USSR Academy of Sciences (it turned out to have belonged to M.V. Lomonosov) with samples of smalts, work was resumed. An ad hoc committee had been formed at the HIT to elaborate the methods and supervise the restoration, which was headed by N.P. Tikhonov. The work actually carried out by a professional mosaic artist, V.A. Frolov, who worked on invitation. The restoration had been completed by January, 1934, and the members of the committee endorsed the correctness of the restoration procedure²⁾. A special historical and technological investigation carried out by the Institute workers made it possible to reproduce the original mosaic technology developed by M.V. Lomonosov.

Restoration of the finds from P.K. Kozlov's collection in Mongolia and Noin-UI (received from the State Academy of the History of Material Culture) continued. Important results had been attained with V.N. Kononov's studies in paint restoration on ancient fabrics taken from these collections³⁾. He also described the methodological procedure for determining a number of dyes, which could be carried out with microsamples and required no complex chemical equipment.

Unique Efench manuscripts of the 13-14th century, adorned with miniatures, which had been received from the library of the USSR Academy of Sciences in dreadful condition (soaked with moisture and covered with mildew, they were glued into a single ball after drying), had also been successfully restored after complex operations.

The second exhibition of the Institute, in May, 1932, organized by the State Academy of the History of Material Culture, was dedicated to the All-Russia Archaeological-Ethnographical Symposium⁴⁾. The exhibit was divided into two sections: the methods of scientific analysis and their practical implementation illustrated on concrete materials from museum funds⁵⁾. The exhibi-

1) Soobshenie GAIMK No 11/12. 1931, p. 43-51.

2) PIDO (Problems of History of Pre-capitalist Societies), No 9-10, 1935. Moscow-Leningrad, 178.

3) Soobshenie GAIMK, No 7-8, 1932, p. 73-74.

4) Ibid., p. 50-54.

5) Ibid., p. 50-54.

tion confirmed the previously adopted line, and demonstrated its practical implementation in the practical work carried out by a number of museum and scientific establishments. The exhibition displayed articles from the State Hermitage, the State Russian Museum, the State Tretyakov Gallery and the Central Restoration Workshop.

Due to reorientation from archaeological objects to the history of technology, the Institute studied water supply technology in the ancient Crimea, fortification technology and even the history of the steam engine. The Institute also dealt with an important problem of practical value - the use of local mineral deposits (analysis of the areas where non-ferrous metals were mined, an historico-technological study of ancient metals, dyes and fabrics), along with investigations of construction materials and construction technology in the Middle Ages in Central Asia and construction processes in Ancient Rus (Novgorod and Pskov)¹⁾. Long-term studies carried out by N.M.Bachinsky in Central Asia made it possible to discover one of the secrets concerning the seismological stability of ancient monuments, which proved immensely important to modern construction in Central Asia²⁾.

Recognizing the scientific importance of monument restoration, the State Academy of the History of Material Culture sponsored a team headed by A.P.Udalenkov, a prominent architect, within the framework of the Institute, whose main task was the compilation of plans for restoring separate objects or whole groups of ancient monuments, and control over actual work (Novgorod, Pskov, Bahchisarai, Ashkhabad, Hersones).

Mounting restoration work on a national scale required trained personnel. In 1936, the first classes in theoretical and practical restoration of archaeological objects were organized for 4th-year students of Leningrad University's Department of History by the Institute's Department of Restoration and Conservation³⁾.

The Institute of Archaeological Technology (as it was re-named in 1937) existed only until 1938. It is impossible to overestimate its role in the development of scientific restoration. The Institute of Archaeological Technology can be rightfully considered the predecessor of the All-Union Research Institute of Restoration and other research restoration establishments in the Soviet Union.

1) Institute of Archaeology (Leningrad Branch) of the USSR Academy of Sciences, Archives. F. 2, op. 1. 1935, 18-133.

2) Ibid., 1936, 211-58. "Anti-seismic Measures of Central Asian Architects in the 15-17th Centuries", was published by N.M.Bachinsky in 1934 (PIDO), No. 5).

3) Institute of Archaeology (Leningrad Branch) of the USSR Academy of Sciences, Archives. F 2, op. 1, 1936, 211-72-73.

Working Group 12

Care of Works of Art in Transit

Protection des oeuvres d'art pendant
le transport



MEMBERS

Elisabeth Batchelor (USA)
Stephen Bonadies (USA)
Gary Carriveau (USA)
Karen Coote (Australia)
Timothy Green (UK)
Stephen Hackney (UK)
Cees van den Meiracker
(Netherlands)
Teri Oikawa-Picante (USA)
Barbara Roberts (USA)
Christine Leback Sitwell (UK)
Deborah Stewart (Canada)
Dla Westerudd (Sweden)

TRIENNIAL OVERVIEW

Coordinators
Sarah Staniforth (UK)
Peter Wilson (UK)

Assistant Coordinator
Peter Cannon-Brookes (UK)

PROGRAMME 1984-1987

1. Research into design of packing cases. Performance testing under controlled conditions and during transit. The aim of this work will be to produce a specification for packing cases suitable for international loan exhibitions.
2. Research into the performance of vehicles used for the transport of works of art. Recording of shock and vibration levels experienced during transport inside the various types of vehicles used by museums. The aim of this work will be to produce a specification for vehicles suitable for transporting works of art.
3. Research into the relation between shock and vibration and the resultant damage experienced by paintings.
4. Investigation into new cushioning methods.
5. Study of particular problems of handling and transporting contemporary art, ethnographical collections and other special categories of exhibit.
6. Production of standard questionnaire for access and display facilities and a draft schedule for checks to be made by couriers.
7. Production of criteria for arbitration of depreciation claims stemming from transportation and environmental damage.

SUMMARY

During 1986 the Coordinator and Assistant Coordinators swapped places, as Peter Cannon-Brookes moved to a new job which no longer involves him in work relevant to the activities of this working group.

A Newsletter was circulated to nearly 90 people who are on our working group mailing list in October 1986. Two more will be published in 1987. The members of the working group have fallen into two sections. The names listed here are those who are actively involved in research relevant to the groups activities. The other 75 are interested in the problems which the group addresses, but are not actively involved in research.

In April 1986 a meeting was held at the Getty Conservation Institute, to prepare a paper on the key issues and questions to be resolved for the safe transport of works of art. Of the five members of the 'Art in Transit Steering Committee', three are active members of this working group. It was agreed that as the aims of the Steering Committee and this working group are so similar, the research that results from the Getty Conservation Institute initiative should be reported through the forum provided by the ICOM Committee for Conservation meeting in Sydney. We hope that this cooperation will continue for the next three year period.

In addition to research topics identified at the 1984 Copenhagen meeting, two papers have been offered on subjects of sufficient interest to be included in this meeting. One is on instructions for non-specialist staff on the handling and transport of exhibits, and the other is about a literally 'travelling' exhibition, in which the exhibition is displayed within the vehicle which moves it between several locations.



SUMMARY

Following previous studies, packing cases for oil paintings were tested to assess a variety of packing materials. This led to some useful practical results. In addition, by monitoring the canvas directly it was possible to measure the accelerations experienced by the paint film. Some further insights were gained into canvas vibration and it was shown that crack patterns could be generated in paint films by the levels of shock and vibration experienced in transit.

SHOCK AND VIBRATION - TEST RESULTS FOR FRAMED PAINTINGS ON CANVAS SUPPORTS.

Timothy Green

Conservation Department
Tate Gallery
Millbank
London SW1P 4RG

INTRODUCTION

It is only during the past fifteen years or so that paintings have been loaned in the numbers we now take for granted. This period is short indeed when compared to the length of time we hope a painting will survive. As yet, little deterioration has been reported. However, future generations would have cause to judge us harshly if the long term effects of repeated transportation turn out to be seriously detrimental to the structure of paintings.

In the short term paintings have proved their resilience. If this were not so, insurance claims would have quickly reduced the number of exhibitions, especially as the monetary value of paintings is so high.

Insurance claims are made when visible damage occurs during a loan. A weakening of structure during a loan that is not apparent initially but manifests itself at a later date may also occur. It is unlikely that this deterioration would be traced to its real cause.

Our lack of knowledge in this area hinders decision making when loan requests are considered. Many conservators, on being asked to advise, are understandably cautious, recognising the importance of mounting exhibitions, but feeling intuitively that the more a painting travels, the more rapid its subsequent deterioration may be.

When requesting a painting for loan, exhibition organisers require a straightforward yes or no. In reality, paintings exhibit a broad range of fragilities.

At the Tate Gallery, each painting is assessed on its structure and present condition, with reference to written and photographic records. In some cases it will obviously be unsafe to lend. Generally, though, a range of treatments and conservation procedures can be applied to make the majority of paintings fit to travel. Any loose paint will be secured and failing tacking edges repaired. Fitting of the painting in the frame will be improved. A backboard will be attached and when possible the frame will be glazed with an acrylic sheet. Unframed modern works will be provided with travelling frames to facilitate safe handling and packing. Slack canvases will be re-tensioned and possibly supported by a second, loose (not adhered) canvas stretched behind to help prevent impacts against stretcher cross-bars.

In these ways, the loans' programme makes a valuable contribution to the overall conservation of the collections guaranteeing the works requested are examined and given any necessary remedial treatments. This would not usually extend to a major intervention, such as lining, simply to make a loan feasible. The approach of the conservation department then is to try and make the lending of paintings possible and safe.

The most worrying decisions concern requests for oil paintings that are crack free but that have aged to a brittle state. As ageing progresses, crack formation becomes ever more likely.

The forces necessary to produce cracking of such films and their relation to the conditions encountered during transportation urgently need to be investigated. Probably such general research would never equip us to the extent that the risk posed by transportation to each individual painting could be assessed accurately. In any case, journeys are highly variable in terms of the shock, vibration and environmental conditions encountered. But it is to the basics of the problem we must look initially.

Is it shock, vibration, changes in relative humidity and temperature, or a combination of these factors which are

responsible for initiating cracking? Can cracks appear and grow during long periods following an accident? These are two of the key questions that need to be addressed.

Certainly speculation about the long term effects of today's frantic loan schedules does nothing to improve the credibility of the paintings' conservator.

Background to tests:

About four years ago, the Tate Gallery began a study to assess the protective performance of the standard packing case specification¹. Mechanical testing gave an indication of the levels of shock and vibration that paintings loaned during past years have apparently withstood. Results were obtained measuring peak (pk) accelerations, but only those experienced on the test frame. Following the example of the National Gallery², a lightweight accelerometer (mass 0.5 gram), was obtained and used in the tests reported in this paper³. By attaching the accelerometer to the middle of test canvases, it was possible to observe directly the response to transmitted vibrations. Test canvases were prepared in various ways, (see appendix II), in an attempt to produce damage that could be related to the forces experienced during testing. It was also possible to assess the effect of backboards and glazing. These results are given later. First, though, we will consider tests designed to help us improve the performance of the packing case itself.

The Packing Case

While the question of long term damage is unresolved, common sense dictates that shock and vibration should be reduced to a minimum, working within budgetary limits and practical considerations. Therefore a range of materials was assessed so that the best choice could be made.

For shock, this is straightforward to do. The packing case is dropped from a defined height and on impact, the packing material that produces the lowest peak 'g' gives the best protection.

Impact shocks, though avoidable, produce large forces that packing foams are selected primarily to protect against. Therefore the drop test results are considered first.

TABLE ONE: DROP TEST RESULTS.
IMPACTS AGAINST FLAT BASE

PACKING CASE NO:	FOAM TYPE	DROP HEIGHTS.		
(see appendix I)		152mm(6")	457mm(18")	915mm(36")
1a	POLYURETHANE-POLYESTER TYPE 100mm (4") *	20g **[19.3g]	32g [66.8g]	49g [>100g]
2a	POLYETHYLENE 'PLASTAZOTE' 87mm (3½")	21.8g	34.7g	53.3g
2b	'PLASTAZOTE' 112mm (4½")	18.1g	30.6g	48.5g
3	DOUBLE CASE. POLYETHYLENE 'ETHAFOAM 220' 75mm (3") (total thickness)	16.6g	61.4g ***43.3g	110g
4	(Cardboard exterior) POLYETHYLENE 'JIFFYCELL' 75mm (3")	21.4g [35.2g]	53.9g [80.0g]	93.2g [>100g]
5	DOUBLE CASE. CUSHIONING-AS 1b AGAINST FRAME. INNER CASE SUPPORTED ON RUBBERISED HAIR * Base cushion thickness	12.2g [31.7g]	30.4g [>100g]	52.9g [>100g]

** Pk 'g' as measured on the test canvas.

*** Foam replaced in inner pack with wood batten.
Reduced pk'g' illustrates tandem cushioning effect.

Discussion

No one foam performed exceptionally well. Most usefully, some potential dangers were highlighted. Packing case 3 displayed the phenomenon of tandem cushioning. This can occur when double case systems are used. A bouncing effect is produced when the foam cushion adjacent to the packed item responds out of phase with the outer foam cushion⁴. It is worth stating that the problem is avoided as long as the following criteria are met:

1. The mass of the inner box must be less than one third the mass of the packed item.
2. The thickness of the cushioning in the outer box must be no less than two thirds of the total cushion thickness.

The effect was best illustrated when packing case three was dropped consecutively from 18" (457mm). Initially a large shock occurred (pk61.4g). In the following test, the foam strip supporting the frame had been replaced with a wood batten. A c30% decrease of the impact shock resulted (43.3g). The static loading on the foam had been carefully worked out to achieve good cushion performance. Reference to the foam manufacturer's data shows that in the first drop, pk 'g' was double the predicted value.

In general, the recommended static loadings were followed and the results were close to those expected. This was not so with packing case 4. (see table one), in which the foam was excessively underloaded. The large area of contact meant a loading of only 0.2lb/inch² resulted. From the dynamic performance curves for 'Jiffycell', the resulting 94g is predicted. Efficient cushioning is produced by polyethylene foams at higher static loadings than can be achieved with continuous cushions against the frame's edges. This led to a problem not apparent from the test results. 'Plastazote' density 24kg/M³ was specified to be used in the packing cases for one exhibition. For unforeseeable reasons, the packing cases were left for a week. When unpacked it was found that large paintings in particular had crushed the foam pads by as much as 25% so that a 25mm (1") gap had formed at the top edge. This phenomenon known as 'creep' is non-reversible and clearly undesirable. Experience elsewhere has shown that by specifying a higher density Plastazote, 45kg/M³, the problem should be avoided.

Another feature of polyethylene foams makes their use questionable for air transport. Invariably such foams are closed cell. Should a rapid de-compression occur during a flight, the foam's volume could increase dramatically as the gas within each cell expands, posing obvious risks.

Due partly to these concerns, polyurethane, polyester type foams appear the best choice. But in addition, their use avoids the complications associated with correctly loading polyethylene foams to achieve optimum cushioning.

Compared to the cushioning performance of polyether chipfoam, used until recently in the Tate's packing cases, polyurethane/polyester foam is less efficient. However the chemical stability of chipfoam is uncertain and within the confined environment of a packing case, chemical stability is a prime consideration.

Toppling

Packing cases for paintings tend to be tall and thin, therefore vulnerable to being knocked over. At airports especially, this is the most likely accident to occur since staff are used to handling freight in squatter containers.

Several toppling accidents of this type have been reported to the Tate Gallery by the airlines when the case has been punctured after toppling on the metal stops on the roller bed used to move air freight pallets. Presumably other cases have toppled but without visible damage to the packing case.

Indeed test packing cases that were repeatedly dropped barely showed any signs of the abuse they had received. Routine monitoring of shock levels during transportation would reveal the extent of this problem though this is hardly a practicality at present. An alternative, the use of a shock indicator stuck to the exterior of the packing case, did not perform well in the

tests. On occasions, decelerations well above the stated threshold levels failed to activate the indicators, whereas a tap with a finger produced immediate results. Nonetheless, their cost could possibly be justified by their deterrent value.

The likelihood of this type of accident makes protection against it of paramount importance. Ways to increase the depth of the packing case in relation to its height should always be considered. (A square box is unlikely to be knocked over). For this reason, packing two or more paintings together has this advantage to recommend it. In the Tate's packing case, 100mm (4") thick panels of expanded polystyrene in each of the large faces is specified. Though primarily a measure to provide good thermal insulation, the effect on the resistance to packing case topple is probably a more important justification. To improve this resistance further, the thickness of insulation in the narrow edges at the top and bottom has been decreased by 2 x 50 mm (2 x 2") and for large paintings is sometimes omitted (the packing foam is a quite effective insulating material). Packing cases for large paintings are then more likely to fit into aeroplane holds.

Test Results:

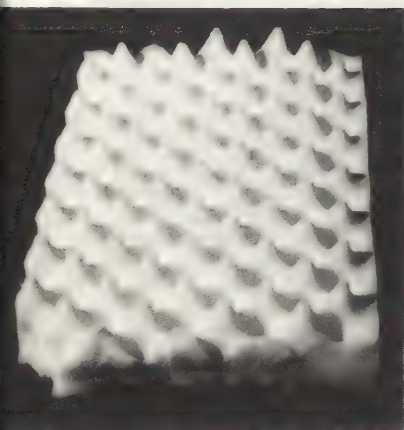
Our first study made apparent the poor cushioning effect of the foam against the front and back of the painting. Therefore the specification was changed. The continuous large face cushions, of polyether chipfoam, were replaced with 250mm (10") wide interlocking strips of polyurethane/polyester foam. From the results in table two it is apparent that this change had produced an improvement, the level of shock now being similar to that measured in the 915mm (36") flat base drop test.

TABLE TWO
TOPPLE TEST RESULTS

N.b: Tests performed by tilting the packing case to a point of balance, then releasing to impact against the large face.

Packing Case No:	Foam type in large faces (as described in appendix I. Any differences as noted below).	Impact against painting face 'F' or back 'B'.	Peak 'g'
1a	In effect 203mm (8") wide strips of polyurethane polyester foam	F	46.1 [90.0g]
		B	57g [>100g]
2a	25mm continuous sheet 25mm corner pads	F	58.1g
		B	70.9g
3		F	72.0g
		B	84.3g
4		F	54.8g [91.5]
		B	42.1g [>100]
5		F	35.9g
		B	30.2g
Additional case to assess convolute foam	37mm (1½") thickness low density polyurethane 'convoluted' foam.	B	39.9g
	Expanded polystyrene foam on case exterior.	B	38.2g

photo 1



Topple Tests, Cushion Performance:

The least resilient packing materials gave the best protection in the topple tests. When convoluted soft polyurethane foam was used (see photo one), the material was sandwiched between the insulation and the inside face of the wooden case. Through the stiffness of the polystyrene panel, the weight of the painting was evenly distributed. To determine whether the good results this arrangement achieved in the topple tests could be improved on, strips of expanded polystyrene were attached at key points to the packing case exterior. These were appreciably crushed on impact, absorbing significant energy. Even so, this barely reduced the reading of peak 'g' experienced by the frame as can be seen in Table two.

Generally, as the importance of correct static loading on the foams had been considered in most of the packing cases tested, reasonably good results were obtained.

VIBRATION

Frame:

It is inevitable that a frame standing on and enclosed by cushioning foam will resonate across a range of frequencies. The foam behaves like a spring with a weight resting on it. At one characteristic frequency, the natural frequency, a peak resonance will occur.

This frequency can be found by carrying out tests on a vibration table. Such tables can produce vibrations across a broad range of frequencies with a constant energy input, usually measured as peak 'g' for each cycle of vibration. During a test, the frame's vibration is monitored. By dividing peak 'g' measured on the frame by the peak 'g' produced by the table, a ratio is obtained. This is continuously plotted during a frequency sweep (3-100 cycles per second, or Hertz (Hz)). When the ratio is greater than one, some resonance is occurring. The highest value will occur at peak resonance, thereby determining the natural frequency for the system under test.

By way of illustration, a trace obtained during a frequency sweep is reproduced in fig (a). This shows a peak resonance of five times the vibration table's 'input' occurring at about 25Hz. It is apparent that as the frequency is increased resonance builds to a peak value and then falls away. When unity is reached, at 64Hz, higher frequency vibrations are reduced or 'attenuated'. The excursion in the trace around 50Hz is caused by the packing-case sides resonating.

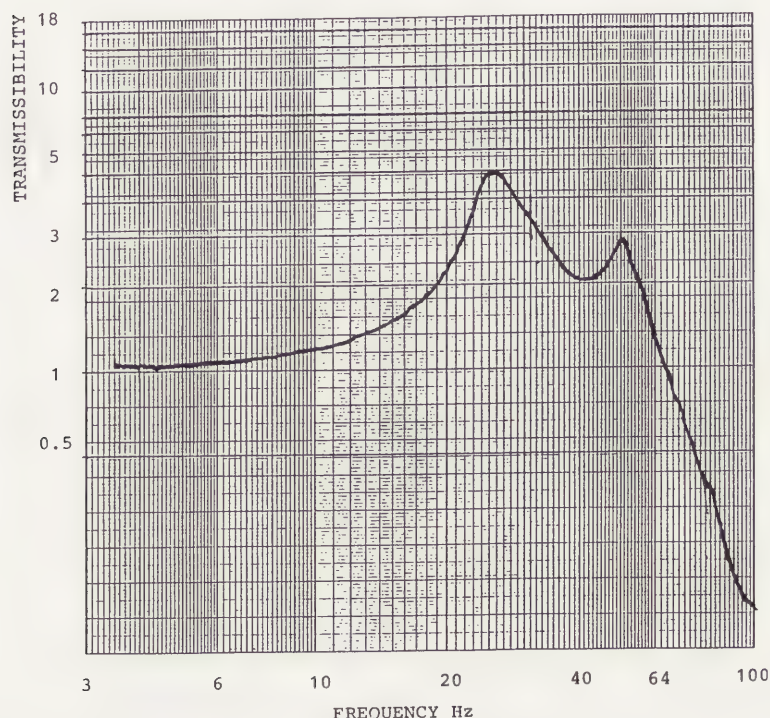


fig a.

One feature of vibration not immediately apparent when considering its acceleration in pk'g', is displacement, the distance through which the item moves during each cycle. Acceleration can be related to displacement by the formulae;

$$a = 0.511 f^2 D \quad \text{or} \quad D = \frac{a}{0.511 f^2}$$

Where a= vector acceleration in gravity units, f= frequency in Hz and D= displacement in inches (double displacement).

The important point is that larger displacements are caused at lower frequencies than at higher frequencies for a given acceleration. So at 2 Hz, a pk acceleration of 1g produces a total movement of about 120mm (4 ") compared to 1.25mm (.05") at 20Hz and 0.05mm (.002") at 100Hz.

In trucks (lorries) large displacements at very low frequencies (>2Hz) are commonplace being caused by the relative unevenness of roads adjacent to the kerb side. It is impossible though to reduce significantly displacements of several tens of centimeters with any packing case system. There simply is not sufficient space within which to isolate the framed painting. Paintings on canvas are quite effectively protected from movements of this type by backboarding and glazing as was shown in our tests, see later. (This protection is less effective at higher frequencies.) Between 10-20Hz, conventionally sprung trucks are reported to vibrate most energetically⁵. Therefore a good foam in terms of vibration response would produce a low frequency peak resonance, say at 3 or 4Hz. By 10Hz the point of unity should have occurred so that higher frequencies are attenuated.

Test Venue and Equipment

The test venue and details concerning the equipment used are described in the reference⁶. For the most recent test series (8/9-12-86) the simulated lorry side was dispensed with. (Previously this stood vertically, bolted to one edge of the vibration table. Packing cases were then secured to it with webbing straps.) This was a possibility as low input accelerations were used (pk 0.3 g, previously 0.7 g). (Wood battens, clamped to the vibration table, held the packing cases so that there was no risk of it falling off.)

From table four, the effect of varying the input can be seen. Results from three frequency sweeps on packing case 1b were obtained using 1.0g, 0.5g and 0.3g inputs respectively. With a reduced input, a greater amplification occurred at peak resonance, but at a higher frequency. Due to this frequency shift, displacement was in fact reduced.

Packing case systems are commercially assessed on their peak amplification value, termed 'transmissibility'. On this basis, lower input accelerations create a more rigorous test.

Research carried out by Art Networks to monitor vibration levels on air ride trucks show, from their results presented at this conference⁷, that low inputs occur (pk 0.1g). So inputs closer to pk 0.1g more closely simulate vibration amplitudes on these vehicles. (Conventionally sprung trucks are known to produce more energetic inputs than this, 8.)

For these reasons we recommend pk 0.3g as a standard input for vibration testing. It is of course necessary to carry out tests in a similar way for results to be directly compared.

Discussion

From the test results (see table 3) it was evident that none of the commonly used foams produced a good result as previously defined. Such foams are selected to give good shock protection.

There are materials available with good vibration isolating and attenuating properties. Felt is an everyday example but, as is usually found with these materials, its poor shock absorbing performance limits its use. A whole range of vibration isolating materials is produced. One of these, rubberised hair, was tested in packing case 5 and gave the best result. Even so, only vibrations at frequencies above 18Hz were attenuated, so this material is not ideal.

Other vibration isolating materials are being investigated, and this continuing study will be reported on at a future date.

TABLE THREE
VIBRATION TESTS

Packing foam results:

Packing cases, standing vertically

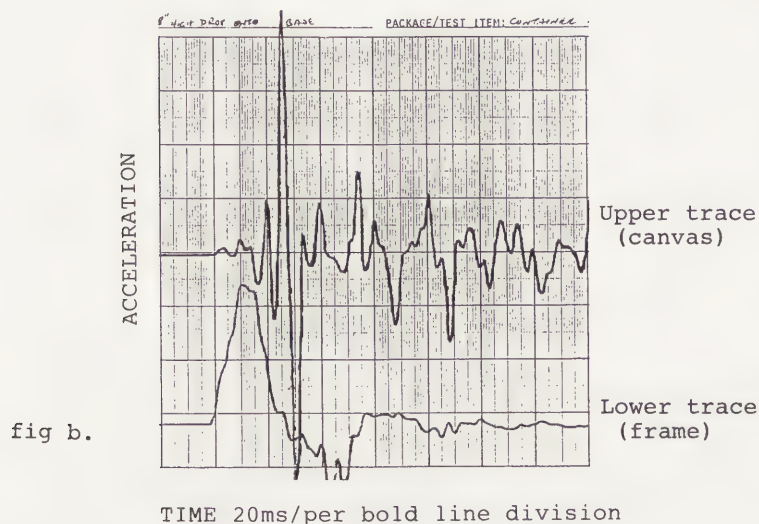
Case no	Pk amplification	Frequency Hz.	Displacement, pk to pk in mm	Input pk acceleration
1a	x1.7	16.5Hz	0.9mm (0.036")	0.3g
1b	x2.7	19.0Hz	3.6mm (0.145")	1.0g
1b	x3.8	22.0Hz	1.33mm (0.053")	0.5g
1b	x4.7	24.0Hz	1.00mm (0.04")	0.3g
2a	x4.8	13.5Hz	8.75mm (0.35")	0.7g
2b	x5.0	17.0Hz	5.75mm (0.23")	0.7g
3	x2.6	22.0Hz	1.25mm (0.05")	0.7g
4	x6.0	31.0Hz	1.15mm (0.046")	0.3g
5	x4.6	9.0Hz	7.5mm (0.30")	0.3g

Vibration Tests

Canvas

When the lightweight accelerometer was purchased by PIRA, it was thought reasonable to allow for values between 0 - 100g to be measured. As is apparent in table one, this scale was often exceeded. In drop tests, vibrations with pk accelerations in excess of 100g were commonplace.

It was possible to store the impact pulse and subsequently to make a trace plotting acceleration in 'g' against time. One example of such a trace is shown in figure b. This was a record of a flat base drop from 457mm (18"). The time base is 20 milliseconds per bold line division, and acceleration is scaled to 20g per bold line division. The lower trace is for the frame, and the upper trace for the canvas.



On impact, the frame was decelerated during 12ms reaching a pk 52.4g, after which it accelerated in the opposite direction (to a peak 24.4g). The canvas, meanwhile, began vibrating but did not develop a high 'g' until some 15ms had passed. One high energy cycle occurred with a peak acceleration of 86.4g. This cycle occurred during about 10ms or 1/100 sec., so its frequency was 100 Hz. A pk to pk displacement occurred of 3.75mm (0.15"). Most other traces revealed that at least four high energy cycles occurred, so the trace in fig. b is slightly unusual. In some drops, the highest pk'g' value was not reached until the third or fourth cycle.

An example of the latter was when the packing case incorporating convoluted polyurethane was toppled. Toppling accidents cause a high deceleration in a direction closer to the axis of the canvases' vibration than occurs with a flat base drop. Even so, there was little evidence in general to indicate that this produced greater canvas displacements. However, with toppling the duration of the high energy vibration was usually longer.

The general conclusion is that, on being dropped, a stretched canvas will not experience one large shock, but rather that a high energy vibration is induced for a short period. Should impact occur against stretcher crossbars or glazing, damage is likely to occur.

From the illustrated trace, it is also apparent that a complexity of interfering wave forms has occurred. This highlights one limitation of the test method used, in that only one point on the canvas was monitored.

In general, similar decelerations were measured at different places on the test frame during any one flat-base drop. This would not be so with the test canvas. If the canvas is likened to a tensioned string that is vibrating, then at its natural frequency, a centrally placed accelerometer would experience a large displacement, but a first harmonic would leave the accelerometer stationary.

To standardise the way tests were set up, the lightweight accelerometer was always attached to the middle area.

In practice this difficulty of interpretation made comparisons of the results from the canvas obtained during drop tests of limited use, but in the vibration tests, because a range of frequency (3 - 100 Hz) was used, the accelerometer invariably experienced significant displacements at some frequency or other. This served more to draw a cautionary note, so that conclusions came from general trends rather than a single result.

VIBRATION ATTENUATION

The effect of backboards and glazing

TABLE FOUR

Test painting no.	How prepared for test	Pk'g'	Frequency Hz	Displacement
3	(1st test) 3mm (1/8") tempered hardboard backboard; 5mm acrylic glazing	3.8g	18.0Hz	5.25mm (0.21") (0.21")
3	(2nd test) 12mm Aerolam aluminium honeycomb backboard	0.56g	20.0Hz	1.00mm (0.04")
3	(3rd test) Expanded polystyrene infill between canvas back and aluminium panel	2.00g	19.20Hz	2.5mm (0.10")
3	(4th test) As above, no EPS infill	2.00g	19-20Hz	2.5mm (0.2")
3	(5th test) No protection	12g	17.0Hz	20.0mm (0.8")
Tests above, performed in packing case strapped to lorry side.				
1b	No protection	14.4g	29Hz	7.75mm (0.3")
1b	3mm (1/8") hardboard backboard	3.45g	32Hz	1.63mm (0.065")

Tests performed with packing case 1b lying flat on the vibration table, painting face down.

Pk accelerations of 12g as measured in the fifth test on painting three were not unusual. At higher frequencies in particular (50-60 Hz) unbacked canvases gave values exceeding 30g on many occasions. In one test, 100g was exceeded. Therefore during vibration testing it was possible to produce pk accelerations comparable to those recorded in drop tests.

Test Results

Dramatic results were obtained when backboards and glazing were assessed. In particular small paintings on canvas were shown to be well protected⁹.

Fitting backboards and glazing to frames are so effective in preventing or limiting damage should vandalism or accidents occur, that other advantages to encourage their use need underlining. Therefore a table of results with some new findings has been included.

Crack formation and development

In the tests performed in Nov 1983, a test canvas was used that had developed a fine crack pattern in the drying of the applied priming, see appendix II. For the Dec 1986 tests this was reprimed to give a crack free surface. During these recent tests, no damage was noted following the vibration tests, but an inspection after the fifteenth drop test revealed a fine crackle in the centre area. (This was the area where the accelerometer was attached to the back of the canvas.)

By the twenty first drop, linear cracks as long as c.150mm (6") were apparent and continued to extend. Distortions corresponding to the inner edges of the stretcher and subsequently cracks were noticed. The final state of the canvas is shown in photographs 2 and 3. As stable conditions (21°C, 50% RH) were maintained throughout testing, the crack system formed as a result of shock and vibration alone.

Similar crack patterns are to be seen on many cracked paintings on canvas supports. The long cracks related to the inner edges of the stretcher bars are especially familiar.

Work is continuing to relate the brittleness of the test priming to that of aged lead white ground on canvas.

Conclusions

Most usefully it has been shown that a crack system characteristic of aged oil paint films on canvas can be produced by shock and vibration. Variations in temperature and relative humidity (RH) played no part as stable conditions were maintained (21°C, 50% RH).

It would now be helpful to determine whether vibration alone can produce this effect since vibration is an inevitable occurrence when paintings are transported, high energy shocks are not.

It was demonstrated in our vibration tests, however, that surprisingly high peak 'g' values can develop at resonance (pk>100g). This high level exceeds that obtained during many of the drop tests.

Backboards and glazing were shown to reduce large displacements of the canvas at low frequencies (<20Hz) especially for smaller paintings.

'Tandem cushioning', found to occur in one carefully designed packing case showed the importance of carrying out testing. The problems caused by underloading cushioning foams were also illustrated.

Hopefully descriptions of the way tests have been carried out and tables of some of the results will prove useful to others wishing to assess a packing system.

photo. 2

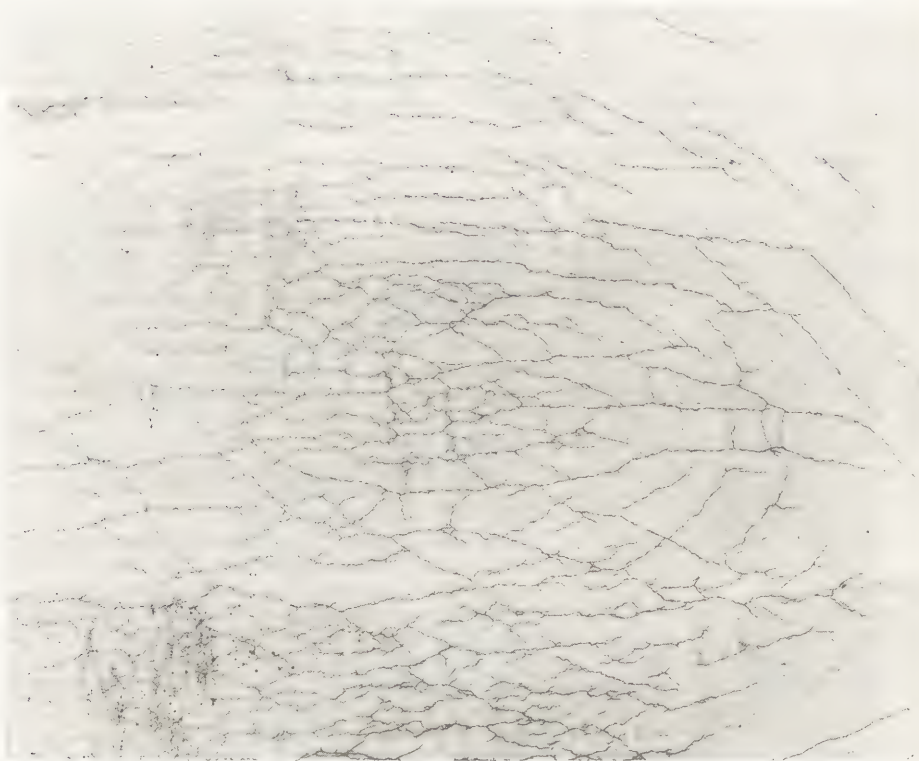
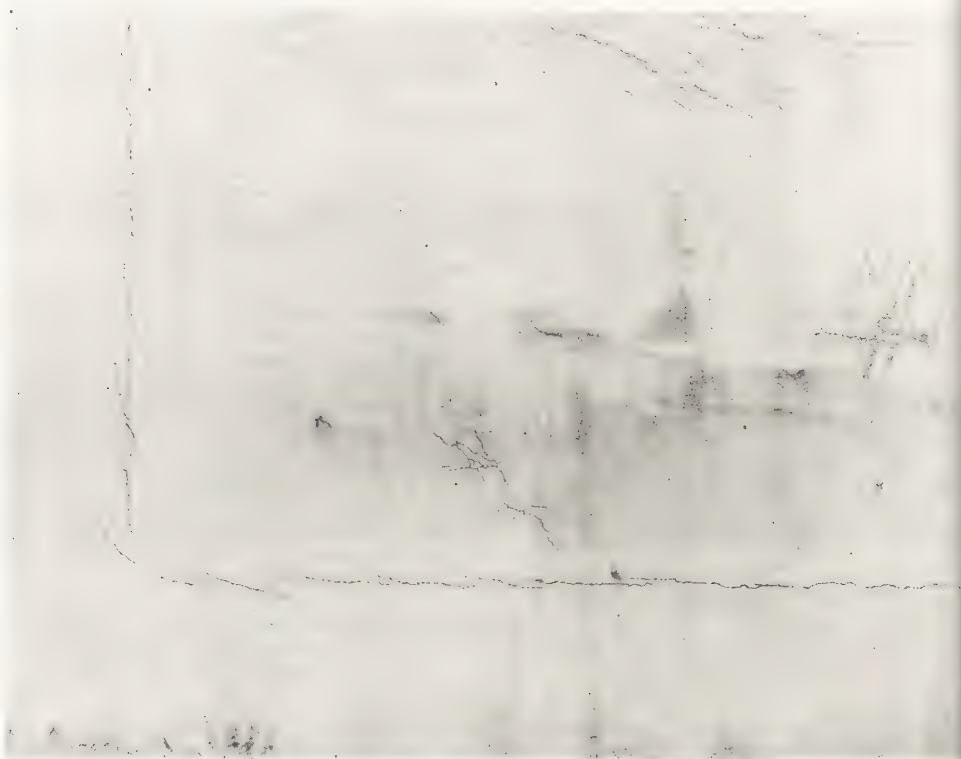


photo. 3



APPENDIX IPacking cases tested:

1. Tate Gallery wooden packing case, incorporating;
 - a. polyurethane/polyester type foam, density 31-33 kg/M³. Cell count 25-35 cells per 25mm (1"). 100mm (4") thickness beneath load-bearing edge, (base cushion) 50mm (2") against other five sides.
 - b. polyether foam 20mm (.78") throughout, laminated to polyurethane - polyester type foam, 22-24 kg/M³. Cell count 25-35 per 25mm (1"). Base cushion 90mm (3½") thickness, other sides 40mm (1½") thickness.

Continuous cushions used in a and b. Open cell foams.

Test performed with Painting One, (T.P.1) see appendix II for details of structure.

2. a. Wooden packing case incorporating 'Plastazote' polyethylene foam, density 24kg/M³. Base cushion, 87mm (3½") total thickness, 50mm (2") thickness, continuous strips, 37mm (1½") thickness pads. (¼ length of frame edge divided into three pads of equal length, one at each end, one placed centrally).

Other sides, 62mm (2½") total thickness, 25mm (1") thickness, continuous strip 37mm (1½") thickness pads. T.P.2.
- b. Foam type and distribution, as in 2(a) - but an additional 25mm (1") thickness of Plastazote on four narrow edges. Closed cell foam. T.P.3.
- c. Packing case, 2(b) base cushion replaced with 75mm (3") thickness 80-90 kg M³. 6-8 lb/ft³ polyurethane chipfoam. Open cell foam. T.P.3.
3. Double case. Outer box, wooden. Inner container, soft-wood edging, 'Fomecore' faces. Inner container supported on 50mm (2") thickness 'Ethafoam 220' mouldings - polyethylene foam. Frame supported 50mm (2") thickness Ethafoam 220, pads against all six faces. (Pad size to give a static loading of 11lb p.s.i.). T.P.4.
4. Cardboard 'Tri-Wall' outer box. 25mm (1") low density polyurethane foam laminated to 50mm (2") thickness 'Jiffycel' polyethylene foam. T.P.1.
5. Double case. Both cases, wooden. Cushioning against frame, as in 2a. Inner case, pads against all six faces 50mm (2") thickness) rubberised hair. T.P.1.

Note: Packing cases 1 a & b, 3, 4 & 5 tested in December 1986.

APPENDIX II:
TEST PAINTINGS

No. Dimensions						Preparation
Frame (H)	(W)	Test Canvas (D) (H)		(W)	(D)	Test canvas, used in first test series (Nov.1983), primed with acrylic gesso. For tests carried out Dec.1986 canvas re-primed with two brush coats of chalk gesso bound with gelatine. Once dried, gesso saturated with a polycyclohexanone varnish.
1. 840mm	980mm	110mm	635mm	762mm	12mm	
(33½")	(38½")	+25mm (4" +1")	(25")	(30")	(1/2")	
2. 1143mm	1458mm	63mm	864mm	1170mm	25mm	New linen canvas, two applications of plaster of Paris.
(45")	(57")	(2½")	(34")	(46")	(1")	

3.	1003mm (39½")	1194mm (47")	76mm (3")	802mm (31")	993mm (39")	19mm (¾")	New linen canvas, two even applications, traditional chalk gesso bound with gelatine.
4.	622mm (24½")	762mm (30")	76mm (3")				Traditional oil painting, 'Pastoral Scene', already cracked.
5.	1467mm (57")	2240mm (88")	14mm (½")	1264mm (49")	2035mm (80")	32mm (1 ¼")	Traditional oil painting on linen canvas, already cracked.

NOTES

1. T. Green and S. Hackney, "The Evaluation of a Packing Case for Paintings", (Paper delivered at the Seventh Triennial Meeting of the International Council of Museums Committee for Conservation, Copenhagen 1984), 84/12/1-84/126.
2. S. Staniforth, "The Testing of Packing Cases for the Transport of Paintings", (Paper delivered at the Seventh Triennial Meeting of the International Council of Museums Committee for Conservation, Copenhagen 1984), 84/12/7-84/12/16.
3. Ibid., 84.12.12. 3.4
4. C. Sitwell, "Results from Shock Testing", (Paper delivered to the United Kingdom Institute for Conservation one-day meeting, June 21, 1985), p.16.
5. B. Georgiou, "The Hazards of Vibration during Transport", (Paper delivered to the United Kingdom Institute for Conservation one-day meeting, June 21, 1985), p.8.
6. T. Green and S. Hackney, "The Evaluation of a Packing Case for Paintings," 84.12.3.
7. C. Sitwell, "Vibration Test Results on an Air Ride Suspension Vehicle and Design Considerations for a Racking System" (Paper to be delivered at the Eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, 1987).
8. Op.cit., B. Georgiou, " The Hazards of Vibration during Transport".
9. T. Green, "Observations on the Vibration of Canvases", (Paper delivered to the United Kingdom Institute for Conservation one-day meeting, June 21, 1985), pp 14-15.

SUMMARY

This paper is concerned with the dimensional stability of the hygroscopic materials in a painting during transit and loan. It emphasises the need to consider moisture content rather than relative humidity in the design of packing systems and to ensure that equilibrium moisture content remains constant.

THE DIMENSIONAL STABILITY OF PAINTINGS IN TRANSIT

Stephen Hackney
Conservation Department
Tate Gallery
Millbank
London SW1P 4RG

Introduction

In transit a painting will probably be packed in a case to protect it from the external environment which may change dramatically during the course of the journey. External relative humidities anywhere between 10% and 100%, temperatures between -20°C and 40°C, and changes in air pressure of 250m bar have to be allowed for.

How effective are the systems we use to protect our loaned painting and can we define more exactly the conditions we would like to maintain?

The Enclosed Case

If we assume our painting is to be transported in an insulated packing case intended to protect it from the worst shocks and vibration and reasonably well sealed to exclude rain, it is possible to predict quite accurately how the interior of the case will behave. Three important papers were written in 1964-66 and an earlier one in 1959 (1,2,3,4). All concluded that well sealed containers filled with hygroscopic material kept at constant temperature would maintain a constant relative humidity and hence moisture content for an enclosed painting. This conclusion has influenced attitudes of conservators everywhere and has prevented much unnecessary damage to paintings on exhibition, in storage and in transit. The principle has formed the basis of the design for packing cases at the Tate Gallery as well as our framing policy.

In a well sealed packing case the relative humidity of the enclosed air is controlled by the fabric and contents of the case since there is far more moisture in these hygroscopic materials than in the air. To illustrate, here is a typical example of a framed painting wrapped in polyethylene.

For a painting and frame weighing 14kg (made up of say 12kg of wood) of dimensions 840 x 970 x 115mm wrapped directly in polyethylene, the total enclosed volume is about 0.10 cu. m. About .020 cubic metres are occupied by wood. The remaining 0.080 cu. m. is air which at 50% RH and 20°C contains about 0.6g of water vapour.

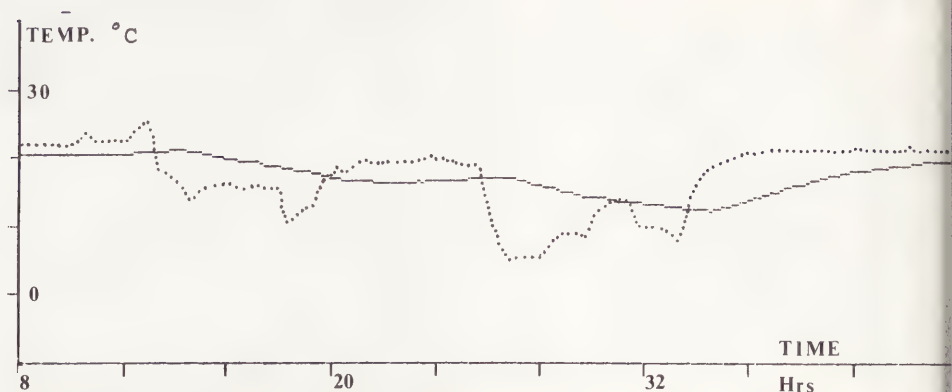
12kg of wood at 50% RH and 20°C contain about 11% of moisture, that is, 1.3kg of moisture. Therefore our framed painting contains 2,000 times the quantity of water that is in the air surrounding it, and this water is in equilibrium with its surroundings.

A complete air change that replaces the enclosed air with fresh dry air would result in the loss of 0.6g of water vapour, causing a 0.6g change in the EMC of the painting and frame. That is a 0.05% loss of moisture content. Surrounded by packing foam and a wooden case the amount of moisture available in hygroscopic material is even greater, perhaps 10,000 times that in the air. It is hardly surprising that the RH in a packing case remains so constant.

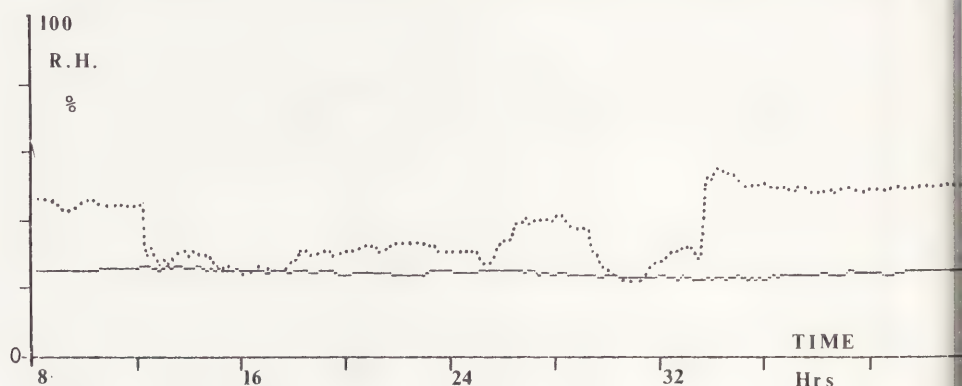
Mass of water vapour in saturated air in grams per cubic metre.

Temp. °C	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
-20	0.89	0.81	0.74	0.67	0.61	0.56	0.50	0.46	0.41	0.37
-10	2.15	1.98	1.81	1.66	1.52	1.40	1.28	1.18	1.08	0.98
- 0	4.84	4.47	4.13	3.81	3.52	3.24	2.99	2.75	2.54	2.34
+ 0	4.84	5.18	5.54	5.92	6.33	6.76	7.22	7.70	8.22	8.76
+10	9.33	9.94	10.57	11.25	11.96	12.71	13.51	14.34	15.22	16.14
+20	17.12	18.14	19.22	20.36	21.55	22.80	24.11	25.49	26.93	28.45
+30	30.04	31.70	33.45	35.28	37.19	39.19	41.28	43.47	45.75	48.14

Smithsonian tables



Temperature inside --- the inner polyethylene wrapping and outside a packing case during transit across the Atlantic Ocean by aircraft. The temp. half-time of the case is 10 hours.



Relative Humidity inside --- the inner polyethylene wrapping and outside the packing case during transit across the Atlantic Ocean by aircraft.

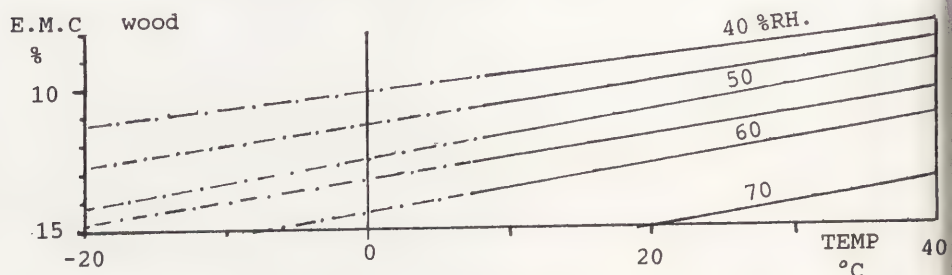
The painting inside the case had been displayed in poor conditions and allowed to come into equilibrium with a very low R.H. during the loan period. It was packed at this low E.M.C. and retained its low E.M.C. in the case during the journey and for several weeks afterwards. The corresponding R.H. is low but very stable despite the continuously higher ambient R.H. outside.

Equilibrium Moisture Content and Temperature

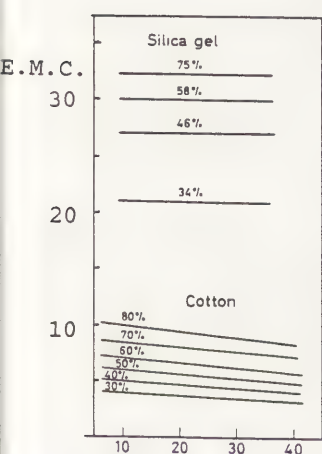
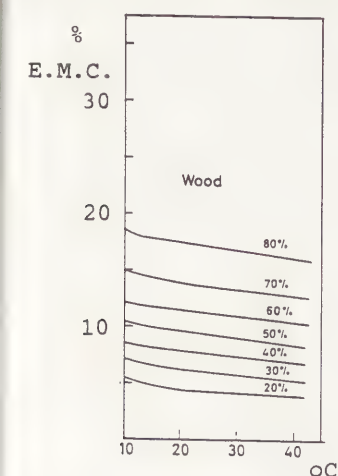
Stolow (2) in particular provided much useful experimental data and also tested some of the theories of the enclosed packing case. Stolow, Thomson (3) and Padfield (4) were principally concerned with stabilising relative humidity at constant temperature. This is well explained by the authors who were considering display cases in heated buildings (Thomson and Padfield) and packing cases travelling in heated lorries (Stolow).

However, it is also worth considering what happens to our enclosure when the temperature changes dramatically. This is a serious question for lenders when paintings may be delayed in transit perhaps for administrative reasons in an airport or by the mechanical failure of a vehicle. To understand what happens it is better to consider the most fundamental property, dimensional stability. If we make the approximation that the coefficients of thermal expansion of the materials in the case and painting are very small and therefore can be ignored, then to ensure dimensional stability we must maintain a constant moisture content for any hygroscopic material.

the relationship between
Equilibrium
Moisture Content and
Temperature at
constant R.H.



Water vapour isobars
for wood, cotton and
silica gel at different
constant R.H.'s. (Stolow)



E.M.C. against temperature

Stolow provides data on the relationship between Equilibrium Moisture Content and RH. The term β (the absolute value of the slope of the E.M.C./ Temperature graph at constant R.H.) shows the change in this relationship with temperature. For most organic materials such as wood, cotton and paper, the value of β is about 0.05 or greater. At high temperatures the moisture equilibrium moves towards the air. For a given RH the material can hold slightly less moisture. Conversely at low temperatures the material will hold more water. According to Thomson's figures wood stabilised to a moisture content of say 12% will be in equilibrium with air at 64% RH and 40°C. Extrapolating to -20°C, the same wood would be in equilibrium with air at 42%RH. Silica gel or polystyrene by contrast have β values very close to zero so they remain in equilibrium with the same relative humidity at each temperature.

A case filled with silica gel that is allowed to go to extreme temperatures will maintain a constant relative humidity but any smaller wooden objects sealed inside will have undergone a change in moisture content. Heating such a case conditioned to 57% R.H. from 20°C to 40°C (for example, if it were left out in the sun) will cause a 1.5% loss in the moisture content of the enclosed wooden object say from 12%-10.5%, equivalent to an RH of 47% at room temperature. A continuous record of relative humidity in transit would not reveal the change in moisture content.

Recently conservators have become aware of the crucial importance of the glue size layer used to seal canvases. In order to ensure a constant moisture content in the glue size layer of a painting exposed to extremes of temperature it is safer to surround it with material of similar β value.

Stolow did not measure the relationship between RH and EMC at different temperatures for gelatine so we have now done so. The result shows a temperature variation similar to those for wood and cotton. We also measured it for linen canvas and polyurethane foam. Linen as might be expected also behaves somewhat like cotton. For polyurethane foam is negligible (like polystyrene) although polyurethane is significantly more hygroscopic. Some more work is being carried out to refine these values since they do not remain constant over the entire range of possible temperature variation. It is hoped to present these results later.

Equilibrium

But all this assumes an equilibrium is maintained between the air and the materials. What is the response time of the wood, canvas and glue? Clearly this depends on the surface area to volume ratio and the nature of the materials. Porous materials with high surface area are very responsive. Foams, silica gel, glue, paper and canvas are very quick to respond to changes in the environment. Wood is slower. If the air were suddenly to dry out and the glue responded by quickly giving up some of its relatively small amount of moisture to the air, then a significant embrittlement would occur until equilibrium were re-established. Clearly a serious possibility. So our packing system must be designed to maintain equilibrium conditions (and all materials used must of course be preconditioned).

Thomson has shown that most timber constructed cases leak quite rapidly through the many cracks and flaws in their structure. This is particularly important when a painting is transported by air. The cabin or hold pressure may fall by 250mbar (one quarter of an atmosphere) equivalent to 8,000 feet (2,500m) for an aircraft flying at 30,000 feet with a pressurised hull. As your ears pop on take off, some of the air is being sucked out of the packing case and on landing it is then replaced by the dry air of the aircraft.

Should we seal our cases hermetically? The disadvantage with sealed cases is that they expand and contract with pressure change. This does not seem like a good idea. A case can be quite well sealed, not sufficiently to cope with aircraft pressures but enough to ensure a very low leakage rate at constant pressure. In practice most wooden cases in common use are very leaky. When we tested an empty Tate Gallery case (with no inner polyethylene wrapper) by evacuating the air from inside we were unable to develop any reduced pressure using a pump rated at 20 cubic metres per hour.

Values of β for various

materials

wood	0.063
Cypress	0.13
B.C. fir plywood	0.05
Ten-test	0.03
silica gel	negligible
cotton	0.03
polyethylene	negligible
polystyrene	negligible
linen	0.07
gelatine	0.03
polyether foam	negligible

Wrapping the painting and frame in polyethylene within the case should reduce the rate of air loss and, at constant pressure, the air will be lost much more slowly by diffusion only.

Conclusions

What can we conclude from these observations and can we design some of these conclusions into our packing systems?

We have shown that a measure of relative humidity inside a packing case could, under certain circumstances, be misleading. To avoid such misunderstandings we should always consider the moisture content of the materials rather than RH of the air inside the case.

The relative humidity inside the case is dominated by the hygroscopic materials. For some hygroscopic materials such as wood, glue and cellulose, as the temperature is raised their moisture contents are in equilibrium with air at increasing RH. For other materials such as silica gel, and synthetic polymers the relationship is constant with temperature. Silica gel (suitably preconditioned) should be used only outside the insulation or an inner moisture barrier.

Equilibrium should be maintained in a packing case by preventing rapid heat gain or loss by the use of thermal insulating materials and also air and vapour loss by the use of barriers. Packing cases should be made as airtight as possible without hermetically sealing. The painting frame should be wrapped in polyethylene sheeting or a similar barrier to enclose a small amount of air in equilibrium with the glue, wood and canvas.

If possible the painting should be glazed with acrylic and provided with a backboard to create a further enclosure in order to slow the air change near the canvas and glue. The addition of a hygroscopic material with a fast response-time, similar to that of gelatine, at the rear of the canvas and the sealing of the canvas reverse by an impervious loose-lining or coating would help reduce the rate of response of the glue. These latter precautions are also of value out of the packing case.

If we can follow all of these precautions (and some may be impractical in certain circumstances), the painting will be protected from moisture change during transit more effectively than by the air-conditioning system in either the lending or borrowing institution. Clearly there is some leeway for decreasing the level of protection against changes in moisture content either to reduce costs or to accommodate other forms of protection from less well controlled dangers such as shock and vibration, but in doing so we must be very cautious in our interpretation of the consequences.

References

1. Toishi, K., Humidity control in a closed package, S.I.C. 4, (1959) 81-7.
2. Stolow, N., Controlled environment for works of art in transit. Butterworths, London (1966).
3. Thomson, G., Relative humidity - variations with temperature of a case containing wood, S.I.C. 9, (1964) 153-69.
4. Padfield, T., Control of relative humidity and air pollution in showcases and picture frames, S.I.C. 11, (1966) 8-30.

SUMMARY

Transit tests were conducted on an air ride suspension vehicle to assess vibration levels at various locations in the vehicle over different road surfaces. Measurements were recorded in the vertical, fore and aft and lateral directions. Based on vehicle results, a racking system for transporting paintings is discussed.

VIBRATION TEST RESULTS ON AN AIR RIDE SUSPENSION VEHICLE AND DESIGN CONSIDERATIONS FOR A RACKING SYSTEM

Christine Leback Sitwell
Art Networks
P.O. Box 17, Warminster, Wiltshire BA12 0SU
England

INTRODUCTION

Over the past few years, technical research in the area of shock and vibration during handling and transport has been undertaken by a number of institutions and individuals worldwide. This research has provided valuable data regarding the levels of shock and vibration on cased and uncased paintings and the corresponding physical behaviour of the test canvases. The majority of the research was conducted at various test centres and incorporated the use of vibration tables and mechanical hoists to simulate conditions of transport and handling.

During these tests, certain parameters were established. For example, for vibration tests the cased and uncased paintings were subjected to a frequency sweep between 3Hz and 100Hz at a constant acceleration input of either .2g, .4g or .7g. Although this test system may artificially simulate the range of frequencies which occur during different modes of transport, it does not reflect the complex pattern of frequencies or varying input accelerations which occur during transit.

For example, when transporting works of art by lorry, the input accelerations will vary constantly and certain frequencies will predominate. The type of road surface, the speed of the vehicle and the type of suspension system will influence these factors. In addition, different locations within the vehicle will provide varying results.

Dr. Waldemar Stuhler in his paper entitled, "Schwingungstechnische Untersuchungen an gangigen Kunst-Transportbehaltern (Vibration Examination Regarding Current Containers for Treasures)," discusses the wide range of situations both inside and outside the museum which can increase the stress on works of art. He emphasises in his article that in order to establish and monitor these stresses we need to conduct actual trials on all types of vehicles used in the transport of works of art.

In 1986, Art Networks undertook a series of tests to establish the load platform response spectra of a lorry of the type likely to be used for the carriage of works of art. The objective was to record the vibration spectra at different locations within the vehicle in the vertical direction, the fore and aft direction and the lateral direction. In addition, these recordings were obtained for different road surfaces to compare the response of the vehicle. The data would enable a comparison between the results obtained under simulated vibration testing and those obtained under an actual transit test. Furthermore, it was hoped that it would provide an assessment of those areas of the vehicle which gave the highest readings thus providing guidelines for the positioning of works of art in the vehicle.

In selecting the test vehicle, we decided to assess the performance of an air ride suspension lorry as a greater number of museums are now using this type of vehicle for the transport of exhibitions. The other type of vehicle which we could have tested was the traditional spring leaf vehicle. The results of a comparative test of a moveable leaf spring tandem axle trailer and a fixed position air ride tandem axle trailer had been sent to us by the School of Packaging of the Michigan State University in the United States and based on their report we decided to concentrate on the air ride suspension system. Although a direct comparison between the two vehicles over the same road conditions would have been invaluable, our financial constraints simply did not allow such a comparison.

The test vehicle was a Mercedes D814 air sprung chassis with a thermally insulated van body, measuring 20' (6.25m) long x 7.6' (2.3m) wide x 8' (2.46m) high.

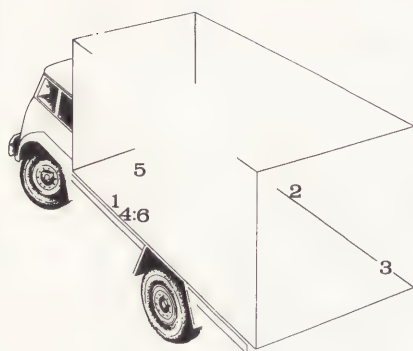


Fig.1 Location of accelerometers in the vehicle

Endevco 2260 accelerometers were located at the following points in the vehicle and recorded vibration acceleration in the vertical, fore and aft, and lateral directions:

- | | |
|-------------------|--|
| Vertical Response | 1. Vehicle floor at 2.3' (.7m) rearward of the left front corner
2. Vehicle floor approximately midway along the vehicle at 7.8' (2.4m) from rear of vehicle
3. Vehicle floor at 1.7' (.5m) forward of rear right corner |
| Fore/Aft Response | 4. Vehicle floor at 2.6' (.8m) rearward of the front left corner |
| Lateral Response | 5. Body side 2.9' (.9m) rearward of left front corner and at a height of 3.3' (1m)
6. Vehicle floor 2.6' (.8m) rearward of the front left corner |

Three types of road surfaces were selected in order to reflect the varying types of road conditions which could occur throughout a journey. They were as follows:

1. A section of a motorway (the M25 motorway near London's Heathrow Airport)
2. A section of a dual carriageway in reasonable repair which was typical of many roads around London's Heathrow Airport
3. A section of a broken and poorly repaired road surface over a motorway bridge

In order to provide a comparison of results for each type of road surface, three separate measurements over each road surface were recorded. The driver attempted to repeat his driving speed for each run but the presence of other cars and the occurrence of traffic lights on the dual carriageway obviously influenced his speed and the degree of acceleration and deceleration. During the measurement recordings, a verbal account of the beginning and end of each measurement period was noted as well as instances of starting and stopping and cornering and sudden braking.

The test results were divided into four categories:

1. Vertical vibration response at locations in the front, mid section and rear of vehicle
2. Fore and aft vibration response in the front of the vehicle
3. Lateral vibration response at floor level at front of vehicle and midway along vehicle at a height of 3.3' (1m)

Due to the lengthy nature of testing and the numerous recordings, we propose to provide a synopsis of the results but copies of the vibration charts can be obtained from the author. The charts show the frequency range between 0Hz and 50Hz (on the X scale) and vibration acceleration recordings on the Y scale (the Y scale is in voltage but a scale of acceleration has been superimposed). Both peak and average readings are indicated. Although peak readings are less frequent, they can do significant damage if they are of sufficient amplitude. During the discussion, we will be referring to peak vibration acceleration.

VERTICAL VIBRATION RESPONSE

Front Floor Location

The main ride frequency motions occur at approximately 1.5Hz for all road surfaces. For the motorway, peak acceleration is slightly in excess of 0.1g at 1.5Hz with peaks of approximately 0.07g at 10Hz-12Hz and 25Hz. The dual carriageway and rough bridge readings show a peak

acceleration of 0.09g at 1.5Hz. For the dual carriageway additional peak accelerations of 0.07g to 0.08g at 9Hz, 12Hz, 24Hz, 26Hz and 29Hz were recorded. For the rough bridge readings, peak accelerations of 0.07g to 0.09g occurred at 3Hz, 9Hz-12Hz and 17Hz-25Hz. For all three road surfaces, there is a frequency band between 4Hz-5Hz at which vibration levels are low.

Midway Floor Location

The readings for all three road surfaces show very little variation from those obtained at the front floor location.

Rear Floor Location

The only significant difference is that the peak acceleration at 1.5Hz is below 0.1g for the motorway trial and slightly above 0.1g for the dual carriageway and rough bridge trials.

FORE AND AFT VIBRATION RESPONSE

Front Floor Location

For all three road surfaces, the peak accelerations were considerably less. At 1.5Hz the peak accelerations were 0.03g-0.05g. For the motorway, peak accelerations of 0.04g occurred at 12 Hz and 18Hz whereas for the dual carriageway similar accelerations occurred at 11Hz, 17Hz, 21 Hz and 25Hz. For the rough bridge trial, peak accelerations of 0.05-0.06g occurred at 10Hz-12Hz, 16Hz-17Hz, 22Hz, 25Hz and 28Hz.

LATERAL VIBRATION RESPONSE

Front Floor Location and Body Side Location

In relation to the acceleration peak at 1.5Hz which had been recorded in the vertical trials, in this trial the peak acceleration was considerably smaller. For both the front floor location and the body side location, the measurements were between 0.02g and 0.05g on the three road surfaces. However, a noticeable peak was recorded at 16Hz at floor level and 12Hz at body side level. For the body side location, peak acceleration was between 0.12g and 0.15g whereas the floor level peak was lower at 0.1g. No doubt the increase in vibration acceleration was due to the flexibility of the sides of the vehicle.

CONCLUSIONS

In general, the fore and aft vibration response tends to be the lowest. This conclusion, however, does not take into consideration the effects of braking. Under normal braking conditions, accelerations up to 0.3g can be recorded whereas emergency braking can cause accelerations up to 0.8g. Vertical and lateral vibration response is similar although the frequency content is different. For vertical vibration, a noticeable peak acceleration occurs at 1.5Hz whereas for lateral vibration response, the peak occurs at 12Hz and 16Hz. The peak acceleration also increases as one moves up the side of the vehicle. In addition, the effects of cornering should be considered as peak accelerations will be higher under those conditions.

When comparing all three directional responses, it appears that the vertical and the lateral vibration responses are greater than the fore and aft vibration response (this excludes any effects caused by braking and cornering). The significant difference between the vertical response and the lateral response is the location of the major peaks. For the vertical response, the peaks tend to fall below 10Hz whereas, in the lateral response, particularly at the body side, the peaks fall between 10Hz and 20Hz. Interestingly, the different road surfaces did not show significant differences. The trials over the rough bridge generally showed a greater number of peaks throughout the frequency spectrum.

When considering these results in view of the location of paintings within the vehicle, it would appear initially that

paintings should be situated laterally across the vehicle as the fore and aft vibrations are lower than the lateral vibrations. However, when you consider braking and the accompanying high accelerations, the placement of canvases in the fore and aft direction is more advisable. The lateral vibration response, however, does indicate that paintings should not be strapped to the sides of the vehicle or at least further testing should be undertaken to consider its effects.

The results obtained during the lorry trials may be of significance in relation to tests conducted on vibration tables. Firstly, the vibration accelerations were significantly lower than the input accelerations used in British test facilities. The lorry recordings showed peak accelerations of 0.1g whereas vertical input accelerations in test facilities have been either 0.2g, 0.4g or 0.7g.

In addition, it was discovered that these accelerations occurred at 1.5 Hz. The frequency range used previously by Art Networks and other institutions at British test facilities began the frequency sweep at 3Hz or 5Hz. Although this may seem a minor point, it may actually be of significance when we consider canvas deflection. If, for example, we measure the vibration acceleration response of a canvas and find two significant peaks of 0.01g at 1.5Hz and 20Hz, the canvas may deflect a distance of about .5" (1.25cms) at 1.5Hz and only 0.03" (.08cms) at 20Hz.

Finally, at test facilities a simulated lorry side is attached to the vibration table but it is possible that this lorry side may be more rigid than the actual sides of commercial vehicles and, therefore, may not reflect a true picture of the vibrational response.

Testing whether it be at a test facility or in an actual transit situation is important because it can only further our understanding of shock and vibration. Test facilities can provide a wide range of valuable data but the data should then be used to provide a basis for test procedures for actual transport testing.

DESIGN OF A RACKING SYSTEM BASED ON VEHICLE TEST RESULTS

Although the major concern of the testing was to establish the load platform response spectra of the vehicle, we were also interested to determine whether or not it would be feasible to design a racking system within the vehicle. Paintings may be cased or uncased during transit. A cased painting may be protected by cushioning material in order to minimise shock and vibration. Unfortunately, it is difficult to select the right material which can effectively respond to both situations as a good shock absorber may be less effective in reducing vibration. Uncased paintings can be vulnerable not only to the effects of transit but also to the effects of handling whilst being loaded and unloaded into the vehicle.

The results of the tests have shown the natural frequencies of the vehicle and have indicated that there is a frequency band around 4Hz to 5Hz at which vibration levels are low. This could be a good frequency to choose for the resonant frequency of a vibration isolating racking system. However, the natural frequencies of the canvas must also be considered and this is a particularly difficult problem to assess.

Art Networks is currently working on the design of a racking system which would consider not only the technical aspects of vibration control but also the practical aspects of safely loading and unloading paintings into the vehicles. To this end we are designing a lightweight aluminium carrying frame onto which the paintings would be mounted. The framework would protect the work during handling and transit and could incorporate a protective covering to protect the works from atmospheric conditions. A vibrational isolating system would either be incorporated in the framework or the racking system itself.

The advantages of such a racking system would mean that individual paintings could be safely housed within a vehicle, particularly as it would prevent paintings from being stacked against each other and then strapped to the side of the

vehicle. As the racking system could be erected and dismantled, it would enable the vehicle to be used for other shipments besides paintings. It would be foolish to think that such a design would be easy to develop and we, therefore, appreciate any comments and suggestions.

(Art Networks would like to thank Burlington Fine Arts, England, for the use of their vehicle for testing and Anthony Best Dynamics, England, for their assistance and analysis of the vehicle recordings. We are also grateful to the Design Council of Great Britain for their partial assistance of the testing.)

BIBLIOGRAPHY

- Georgiou, Bambos, "The Hazards of Vibration during Transport." Paper delivered at UKIC Meeting on Packing Cases-Safer Transport for Museum Objects, 21 June 1985, in London. Preprints
- Goff, Dr. James; Grebe, Joseph; Twede, Diana and Townsend, Todd, "You'll Never See It From the Road-An Examination on the Response of Lading to Transit Excitation by Three Truck Suspensions." Scholl of Packaging, Michigan State University, November 1984.
- Green, Timothy, "Moving Pictures II. Packing for Transport." The International Journal of Museum Management and Curatorship 4, No.1 (March 1985): 45-48.
- Green, Timothy, "Observations on the Vibration of Canvases." Paper delivered at UKIC Meeting on Packing Cases-Safer Transport for Museum Objects, 21 June 1985, in London. Preprints
- Green, Timothy and Hackney, Stephen, "The Evaluation of a Packing Case for Paintings." Paper delivered at the ICOM Committee for Conservation, 7th Triennial Meeting September 1984, in Copenhagen. Preprints
- Leback, Karen, "The Art of Couriering, Shipping and Packing Museum Objects." The International Journal of Museum Management and Curatorship 5, No.2 (1986).
- Mills, Eric, "The Principles of Shock Protection Systems." Paper delivered at UKIC Meeting on Packing Cases-Safer Transport for Museum Objects, 21 June 1985, in London. Preprints
- Piechota, Dennis and Hansen, Greta, "The Care of Cultural Property in Transit: A Case Design for Travelling Exhibitions." Technology and Conservation 7, No.4 (Winter 1982): 32-46.
- Sitwell, Christine Leback, "Moving Pictures III. Packing: A Range of Alternatives." The International Journal of Museum Management and Curatorship 4, No.1 (March 1985): 49-52.
- Sitwell, Christine Leback, "Results from Shock Testing." Paper delivered at UKIC Meeting on Packing Cases-Safer Transport for Museum Objects, 21 June 1985, in London. Preprints
- Sitwell, Christine Leback, "Shock and Vibration Considerations in Packing Works of Art." Paper delivered at the 10th Anniversary Conference of the Institute of Paper Conservation, April 1986, in Oxford, England. Preprints
- Sitwell, Christine Leback, "Shock and Vibration Testing." Paper delivered at the 5th International Conference of Packaging, October 1986, in Bristol, England. Preprints
- Sitwell, Christine Leback, "Technical and Practical Considerations in the Design of Packing Cases for Paintings." Paper delivered at the American Institute for Conservation of Historic and Artistic Works 11th Annual Meeting, 25-29 May 1983, in Baltimore, Maryland,

USA. Preprints

Staniforth, Sarah, "Packing: A Case Study." National Gallery Technical Bulletin 8 (1984): 53-62.

Staniforth, Sarah, "Packing of Two Dimensional Objects (paintings, prints and drawings)." Paper delivered at UKIC Meeting on Packing Cases-Safer Transport for Museum Objects, 21 June 1985, in London. Preprints

Staniforth, Sarah, "The Testing of Packing Cases for the Transport of Paintings." Paper delivered at the ICOM Committee for Conservation, 7th Triennial Meeting, September 1984, in Copenhagen. Preprints

SUMMARY

created in 1973 to increase access to Canada's national collections, the Mobile Exhibits Programme travels year-round bringing museum exhibits mainly to rural communities which do not have ready access to museum facilities.

display artifacts, works of art, natural history specimens, replicas, models, and dioramas are housed in three caravans, each caravan consisting of three fourteen-meter long custom-fitted highway transport trailers depicting a region of Canada. This paper discusses some of the conservation problems which are associated with road travel. These problems include environmental monitoring, climatic extremes, fluctuating temperature and relative humidity, display dusting, dust and vibration.

CONSERVATION IN THE SERVICE OF MOBILE EXHIBITS

Deborah Stewart
Mobile Exhibits Programme
2785 Riverside Drive
Ottawa, Ontario
K1A 0M8 Canada

History and Description of Programme

The Mobile Exhibits Programme was introduced by the National Museums of Canada in 1973 to further the federal policy of democratization and decentralization. The primary objectives of the National Museums policy were to ensure that all Canadians, regardless of where they lived, would have access to their natural and cultural heritage, and that such heritage be preserved.

Museumobiles were created to meet the specific need of communicating this heritage to the millions of Canadians living away from large urban centers and not served by a museum. They also provide nation-wide information on National Museums of Canada, and technical advice and information on Mobile Exhibits to the museum community and to other interested bodies both nationally and internationally.

The Programme currently operates three museumobiles, each comprised of three custom-fitted 14-meter highway trailers depicting the geological, natural, social and cultural history of three different regions of Canada; the North, the Prairies and the Atlantic provinces. Preliminary storylines and design work have been completed for two additional museumobiles representing the Pacific and Great Lakes/St. Lawrence regions.

The exhibits are designed to be educational and entertaining. Multisensory techniques include the use of artifacts, artwork, replicas, specimens, models, dioramas, photographs, and sound and lighting effects. In addition, mechanical exhibits and computerized games are used to excite the interest of younger visitors and to keep pace with the more technologically sophisticated exhibitry now popular.

There are several aspects which are unique to the museumobile exhibits. A thematic approach is used, with artifacts and other display objects serving as support materials. This is somewhat different from most museums where the exhibits usually revolve around objects in the museum's collections.

Museums and individuals in each region assist in the development of the storyline and in providing artifacts.

A linear design is used so that the visitor enters the front door and walks through every exhibit before leaving. The trailers are arranged in a U-configuration and are joined by bridges and canopies.

Rotating teams of road crews travel with the museumobiles. Each team consists of a tour manager, technical officer, senior interpreter and four interpreters. These teams are expected to perform many duties; they drive and maintain the vehicles, set up on site, meet with the press, present Outreach programmes, give school tours and answer enquiries from the general public. Approximately 60% of the tours are interpreted, and interpreters are available at all times to render assistance and answer questions.

Probably the most unique aspect is the mobile nature of the Programme; the sharing of a museological experience with those in remote areas and communicating the national heritage beyond the National Capital Region. Wheelchair access is available for handicapped visitors and an Outreach programme serves those who are unable to visit the trailers, such as senior citizens, those in hospitals or penal institutions, and schoolchildren who for various reasons cannot visit the exhibits.

The museumobiles travel year-round and have visited all ten provinces and both territories. Each year they collectively receive upwards to 275,000 visitors during 10,000 viewing hours in approximately 175 communities. In 1986 the three-millionth visitor was welcomed and the three museumobiles had travelled a total of 25,000 miles throughout Canada.

Conservation

At Mobile Exhibits the conservator's role is an important and challenging one. The conservator must find and maintain a delicate balance between the sometimes conflicting interests of preservation and public programming.

Because the Programme is not in itself a museum, artifacts and specimens are borrowed from museums in the regions depicted, and also from the National Museums of Canada. Upon receipt of an artifact, its suitability for long-term travel is determined and both written and photographic conservation documentation are carried out.

Undeniably, the rigours of road travel subject artifacts to experiences not normally associated with museum exhibits. Dust, vibration and impact, temperature extremes, and fluctuations in relative humidity are realities which must be considered in advance, and their effects buffered as adequately as possible.

Throughout the year, the conservator visits the museumobiles periodically to monitor the condition of display items, up-date condition reports, check for loose or broken mounts, and to undertake minor treatments if required. No major treatments are undertaken without the prior consent of the lending institution. Damage to loaned items is, fortunately, a rare occurrence. Upon termination of loans, copies of condition and treatment reports accompany the artifacts when they are returned.

In addition to monitoring exhibits and artifacts, trips to the museumobiles help the conservator to maintain a good rapport with the road crews. The crews become the conservator's eyes and ears on the road, and a good relationship is important if information about the exhibits is to be reported.

Road staff are given a two-day Introduction to Conservation seminar to familiarize them with different types and causes of deterioration, basic concepts and ethics of conservation, and also to instill a sympathetic attitude towards museum objects and practices. With this basic training the crews are able to keep an eye on the exhibits, identify problems, and to report any problems or emergencies to the conservator who then advises on the appropriate action to be taken. It is fully understood that no treatment of an artifact is to be undertaken except by the conservator, or under his or her direction. This situation appears to work quite well and several potential problems have been averted this way.

One problem associated with mobile exhibits is that of impact and vibration, particularly during the cold winter months when the effectiveness of the air-ride suspension system is reduced by approximately 20%. When the trailers are on site, vibration may be caused by heating and air-conditioning equipment, heavy winds, and the movement of crowds within the trailers.

Every artifact must be adequately secured as well as supported. All mounting materials must be buffered to prevent abrasion and breakage, and must also permit some 'give'. In addition, G-forces must be considered, particularly for heavy objects. These problems can be illustrated by the mounting of a fossilized skull with monofilament line, a common museum mounting material. If the line is not buffered with a material such as Tygon or polyethylene tubing, it may abrade the skull, causing lines. Conversely, if the skull is stronger or sharper, it may cut through the line. A line with a tensile strength only marginally greater than the weight of an object may stretch under the influence of G-forces, causing the line to slacken.

Dust is a constant problem and comes from many sources. During transit, exhibit construction dust is loosened and shaken down. Because many of the communities visited are in remote areas, many of the roads travelled are dirt or gravel, and dust levels can reach choking proportions. Winds carry airborne dirt and dust, particularly during the summer, and in the more arid regions of the country. In addition, the effects of travel, metal, mechanical equipment and use of synthetic materials do little to discourage the presence of static electricity and 'clinging' dirt. As a result, plexiglas cases, which protect their contents from all but the finest dust, must be replaced on a regular basis as they become scratched from the constant cleaning of abrasive particles.

Climatic extremes and variations create hardships on vehicles, road crews and exhibits alike. In a country as large and diverse as Canada, one may encounter conditions ranging from rain forest to desert and maritime to Arctic, depending on the locality and time of year.

Extreme and sometimes sudden fluctuations in temperature and relative humidity are not uncommon, particularly when the trailers are shut down in the winter during moves and over the Christmas/New Year holiday. The trailers receive their power for lighting, heating and air-conditioning from a diesel-powered generator which is housed in a separate vehicle. During transit the trailers are disconnected from the generator. The generators require daily maintenance and are turned off when the museumobiles are to remain closed for any length of time. During these periods the temperature inside the trailers gradually reaches equilibrium with the outside temperature. When the trailers are hooked back up to the generator, the reverse occurs.

The temperature/Rh problem is compounded by the constant opening and closing of the doors as visitors arrive and depart, although the use of canvas canopies over the doors does prevent wind and direct sunlight from entering. The most stable environment is found in the center of the second, or middle, trailer. Unfortunately, it is not always possible to display the most fragile items here as the artifacts must relate to the storyline, which is chronologically and thematically arranged. Where an artifact is considered too valuable or fragile to withstand these conditions, replicas or purchased items are used.

Touch items are tremendously popular, both with school tours and senior citizens. However, because these items receive a lot of wear and tear and must be replaced occasionally, Mobile Exhibits tends not to use artifacts, but samples of materials from which they are made. For instance, different fur samples are handled, rather than clothing made from them; a piece of baleen is shown rather than a dish made of it, and a slab of soapstone is cut with a knife to demonstrate how easily it can be carved, rather than damage a stone lamp or cooking pot. Coupled with an explanation of how these materials are attained and used, and possibly with a related artifact nearby, visitors are able to participate in a multi-sensory learning experience without further hazards being placed on the artifacts.

For approximately a year and a half, hygrothermograph were used in the museumobiles to try to record actual fluctuations in temperature and Rh. This practice was eventually discontinued due to the fragility of the units, their unsuitability for travel, and the need for regular maintenance and calibration. Because the units had to be carefully packed away during moves, data is unavailable for the times when fluctuations were probably at their greatest. For the past year, the Canadian Conservation Institute has been working on a shock-absorbing mounting system so that hygrothermographs can be permanently installed and continuously operated in a vehicle, without being affected or damaged by impact and vibration.

The Mobile Exhibits Programme is hoping to initiate an environmental study to deal with these problems once and for all. The objectives of this study would be two-fold:

- 1) To find a viable and accurate method of continuously monitoring temperature and relative humidity 365 days of the year. Ideally this method would be relatively inexpensive over the long-term, be maintenance free, be visually unobtrusive so as to be used simultaneously inside and outside exhibit cases for comparative data, and be unaffected by the rigours of road travel.
- 2) To determine both short and long-term methods of environmental control. This would involve testing the effectiveness of additional insulation, hygroscopic construction and display materials, and the use of non-granular Rh buffering agents such as Art-Sorb, in both simulated and actual conditions. In future, the possibility of independent power sources for each trailer, and the use of both a thermo and humistatically-controlled air-conditioning system will be investigated.

Conclusion

Since its inception in 1973, the Mobile Exhibits Programme has established itself as an important federal museological service to all Canadians. Through the use of this type of exhibitry, even those living in remote areas are able to enjoy and share in their national heritage.

Anticipating the needs of each artifact, reducing risks wherever possible, regular monitoring of the exhibits, and prompt action when problems arise, have guaranteed that Mobile Exhibits has not become a consumer of collections. In fact, it has been the experience of the Mobile Exhibits conservator that display items have remained in remarkably good condition considering the rigours to

which they are exposed. Although a conservator's responsibility is first and foremost to ensure the continued well-being of artifacts, it is also recognized that sometimes other demands must be placed on objects if they are to be of value to a culture or society.

By finding and maintaining an equal balance between these two roles, the Mobile Exhibits Programme is ensuring that Canada's national collections can be enjoyed today and will be here tomorrow.

TRANSPORTATION AND HANDLING OF ART AND OTHER EXHIBITS

Ola Westerudd
Jönköpings läns museum
Box 2133
S-550 02 JÖNKÖPING
SWEDEN

Summary

It is a known fact that a lot of the damage done to our museum exhibits is caused by museum employees themselves, mostly during the transportation and handling of objects. Ignorance of these matters is of course more widespread in regional and local museums than in national ones.

A study group taking part in the Swedish Museum Association's Conservation Planning project has drawn up standards and instructions for regional and local museums on the transportation and handling of pictures, furniture, glass and china. This work has resulted in sets of slides with separate printed booklets containing monochrome illustrations. The present article describes the background, how the slide sets were produced, how they have been presented and the importance of entrusting this work to an expert. The aim is, using simple means and materials, to protect art/other exhibits from unnecessary damage in transit and during handling.

As part of the same project, a similar booklet has been compiled on the handling and storage of textiles. This is unaccompanied by slides but is more comprehensive than the other booklets. The textile booklet, however, is presented in another context.

Introduction

This paper is a presentation of simple precautions for the transportation and handling of pictures, furniture, light fittings, glass, china etc. In choosing simple methods and materials, our aim has been to advise and instruct regional and minor museums, local history associations, national, municipal and other public institutions and organisations, and persons handling art and objects of cultural interest in a private capacity.

Finally, an account will be given of experience gained from the presentation of these slide sets and booklets.

Background

Some years ago, the Swedish Museum Association, an interest organisation representing all museum personnel categories in Sweden received from the National Council for Cultural Affairs, which is directly responsible to the Government, a grant for a conservation planning project. The aim of

the project is to improve the knowledge of all museum personnel categories concerned with museum collections, but also to improve the co-ordination of storage and conservation measures. The nucleus of the project consists of four study groups set up at the museums to penetrate four important problem sectors. These groups include both conservators and armoury curators, store-keepers and keepers, as well as outside experts.

Progress reports have been distributed continuously to all the Association's member institutions. One of the study groups has compiled sets of colour slides accompanied by booklets with similar pictures in black and white, as part of an in-service training programme on the transportation and handling above all of museum exhibits. Another group is drawing up recommendations on climate and lighting conditions for exhibitions and storage facilities, while a third has drawn up standard methods for assessing and recording the condition and storage of collections. Yet another study group is drawing up plans for an information centre on preventive care in museums.

The slide sets, then, are for people who own, administer, handle and are responsible for art and other exhibits, but who have little or insufficient knowledge of the subject. The aim is to eliminate the grossest errors, to assist in the selection of materials, and to explain where the materials are available and how exhibits should be handled, packed and transported.

More often than not, the layman - but occasionally the professional too - is ignorant of the simplest, most elementary rules and can therefore very easily cause damage.

Activities

The Transport and Handling Study Group numbered up to ten members, scattered all over Sweden, but the group's normal strength is 3-5 persons. We have met in various places besides Stockholm, e.g. at the central depot of the Nordic Museum, 120 km from the capital.

Experts from the central museums in Stockholm have been consulted in their various exhibit fields. Members of the group have themselves drawn up programmes, taken photographs and edited material, written copy and taken charge of layout. The cover design was produced centrally by the Swedish Museum Association.

The first booklet and set of slides are entitled "Transport and Handling of Pictures", the second "Handling and Packaging of Furniture". They are written in Swedish, so the titles referred to here are translations. Both booklets have the same introduction.

They are divided into chapters.

Pictures:

1. Examples of damage.
2. Taking down and stacking.
3. How to carry pictures.
4. Preparations for packing.

5. Packing.
6. In-house transportation.
7. List of materials.

and for Furniture:

1. Storage furniture.
2. Chairs, beds etc.
3. Tables.
4. Gilt objects.
5. Long-case clocks.
6. Light fittings.
7. Loading.
8. List of materials.

The captions accompanying the first pictures also form a brief introduction. The sets comprise 35 and 36 pictures respectively.

The Swedish Museum Association holds an annual general assembly, usually in Stockholm, during what is known as Museums Week. The group's working results have been presented at this assembly, so as to give museum staff an opportunity of critically scrutinising and supplementing our labours. The group then held a further meeting to edit and supplement its production. Finally we asked an outside librarian to examine the captions, to make sure that they would also be intelligible to the layman.

As work progresses, one keeps on learning things. Time and time again one has to remind oneself of the purpose of the sets of slides and the booklets. One has to remember whom one is addressing, one has to take care not to get too technical, not to use material - boxes etc. that is too complicated, because we know from our own experience that convenience, and to some extent time as well, is public enemy no. 1 where careful packing is concerned. A loose blanket, a sheet of paper or a piece of plastic are the sort of aids which people are most willing to use. Sometimes this is enough, but we also aim to show and explain when it is not enough, and also to make sure that materials are used the right way.

Our target group consists, not of professionals at the central museums, though they can also make mistakes, but ordinary museum caretakers, laymen and voluntary workers. We can improve their performance, not by forcing sophisticated methods and aids down their throats but by pointing out the weaknesses of works of art or other exhibits and the easiest but still adequate ways of protecting them in transit. If, in addition, we can induce people to call in museum professionals and others on complicated occasions, we will have cause to be fairly pleased with ourselves.

Results and experience

So much, then, for our aspirations and our target groups. Every regional museum should have a set of slides in each material sector, together with a generous number of booklets.

What happened when we had completed our first set of slides and booklets about preventive care? How was our message received?

When the sets of slides were presented during the 1986 Museums Week, museums were invited and urged to buy the slides and booklets. These were heavily subsidised and the booklets, which sell fastest, only cost about US 3\$.

The members of the group have employed somewhat varying methods of disseminating information. At the regional museum where I work, I presented the sets of slides to the entire museum staff, on a more or less compulsory basis. The advantage of the slides is that, being in colour, they amplify and elucidate the message - the information. People who have only seen the booklets before react positively. Booklets have been issued to the relevant personnel categories at the museum.

Our county also has municipal museums and art galleries. Their staffs have also been convened and briefed about the slides. Most municipal authorities have a cultural affairs committee or officer, responsible among other things for the art which the municipality purchases and administers. All these persons were invited, together with those responsible for the art collections or cultural activities of national authorities located in Jönköping.

The county council, which is responsible for medical care in the county, also has responsibilities for art and cultural affairs, and the relevant county council representatives took part in the conference. The local history associations have already been mentioned as a large and important target group.

They do a great deal of enthusiastic voluntary work on our local cultural heritage, but their knowledge, like their financial resources, is not always equal to the occasion. As a general rule, their collections of iron and wooden exhibits and suchlike constitute larger groups of material than pictures and furniture. They are very anxious to take proper care of their collections themselves, and so a useful purpose can be served by combining these things, the care of a particular category of materials, with the transportation and handling of furniture, for example.

Where these people, most of them farming people, are concerned, it may be appropriate to pass very rapidly over specialised matters in the sets of slides.

Outside the county, the sets of slides have also been shown to prospective museum conservators and art historians.

What response has been aroused, and what is the best way of presenting the programme? As the recipients have not been experts on transport or packaging, the programme series has not excited much criticism or comment, but in my opinion the slides have to be presented by a museum specialist with a knowledge of or responsibility for transport/handling. The audience must have somebody of whom they can ask questions. It is convenient, but not realistic, for those of us who took part in the work of the group to present it all over the country.

In my county certain target groups have still to be contacted - more local history people but perhaps road haulage, removal and auctioneering firms as well.

The Swedish Museum Association Secretariat has also distributed information, articles and appeals to people to buy the sets of slides. The Secretariat operates on a more nationwide basis, but it does not present the product on the spot.

The products are selling well, especially the booklets. The other members of the study group have also presented the slides in their various regions.

At the time of writing, January 1987, another series, "Transport and Handling of Glass and China", is nearing completion, so we are still making headway.

We believe that in most countries it would be useful to broach the idea of this kind of in-service training, training which will also help us conservators to achieve more permanent results than at present. As things now stand, all the work put into an exhibit can be destroyed in next to no time through ignorance of the best way of handling things.



SUMMARY

This paper shows how the risk of toppling of transit cases for paintings may be reduced. Calculations demonstrating the effects of such measures on other aspects of case design are presented. The paper promotes an approach to case design supported by calculation, rather than a wholly empirical one.

MATHEMATICAL PREDICTIONS OF TRANSIT CASE PERFORMANCE; "TOPPLABILITY", THERMAL INSULATION, WEIGHT AND VOLUME

Peter Wilson
Department of Exhibitions and Technical Services
Tate Gallery
Millbank
London SW1P 4RG
United Kingdom

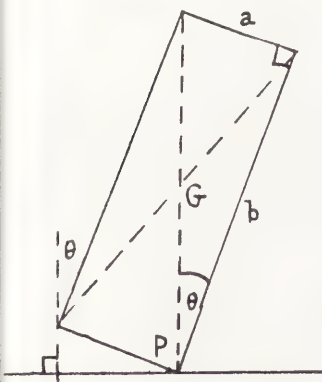
Introduction

In the recent experience of the Tate Gallery, the commonest accident which befalls cased paintings in transit is for the upright case to topple onto one of its large faces. It is particularly hard to design a case to deal with the shocks caused by accidents of this nature and, if the case should fall onto any protruding object (and there are plenty of these in airport cargo handling areas) the results may be catastrophic. Even escorted cases can be vulnerable at airports where, more often than not, access is restricted and liaison less than perfect. It is therefore appropriate to consider what measures can be taken to reduce the "topplability" of transit cases for paintings and to quantify the benefits and disadvantages of various design modifications. This paper serves also as a demonstration of the possibilities of calculation rather than an empirical approach to such modifications.

Calculating the "Critical Toppling Angle"

Figure 1:

Section through a packing case at its "Critical Toppling Angle"



A packing case will topple when it is tilted to such an angle that its centre of gravity, G, is outside the pivot point, P (see Fig. 1). For the moment we shall assume that the packing case is a simple box and that the combined centre of gravity of the box and its contents lies at the intersection of the diagonals (ie. the geometrical centre).

The angle of the case to the vertical, which must be exceeded for toppling to occur, shall be called the "Critical Toppling Angle" (CTA). It is labelled θ in Fig. 1. and occurs when the diagonal of the case is vertical. Reference to Fig. 1 shows that the Critical Toppling Angle is related to the geometry of the case in the following manner:

$$\tan \theta = a / b$$

From the ratio of the depth to the height of this simple box (a/b) we can easily establish the Critical Toppling Angle. We can express the stability of a case not only in terms of the CTA but also in terms of the tangent of that angle, which is the ratio of depth to height. If we set an arbitrary minimum toppling angle of, say, 15° we can look up the value of $\tan 15^\circ$ in a set of mathematical tables⁽¹⁾ and find that the minimum acceptable ratio of depth to height is 0.2679. This provides a simple rule-of-thumb way of assessing stability. It must be emphasized that tall cases become very deep if an angle as large as 15° is used (a 2m tall case would have to be more than half a metre deep!) so different criteria may need to be applied to taller cases.

Let us consider a simple example. A painting of dimensions 1000mm(high) x 1200mm(wide) x 100mm(deep) is packed tightly in a box made of 25mm thick wood with a lining of 50mm of polystyrene insulation. The overall height of the case, b, is

height of painting + 2(combined thickness of wall & insulation)

$$1000 + 2(25 + 50) = 1150\text{mm}$$

The depth of the case, a, is

depth of painting + 2(combined thickness of wall + insulation)

$$100 + 2(25 + 50) = 250\text{mm}$$

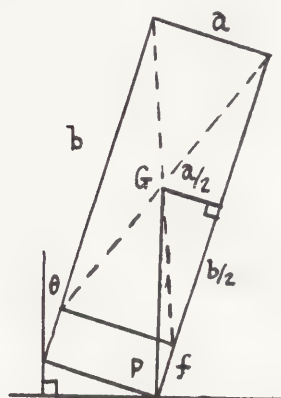
a/b, the ratio of case depth to case height is $250/1150 = 0.2174$, giving a value of θ of 12.3°

Clearly, anything that can be done to increase the ratio, a/b, will increase the CTA. One way in which the ratio could easily

be increased is by increasing the thickness of the insulating lining, which would bring the added benefit of improved thermal half-time⁽²⁾. A case having double the insulation would have a value of a/b of 0.2800, giving a critical toppling angle of 15.7° , an improvement of 28%. Had we increased only the insulation on the large faces to 100mm, leaving the smaller faces at 50mm, a/b would have been 0.3044, equivalent to a CTA of 16.9° , 37% better than the standard case. This latter practice is becoming the norm at the Tate Gallery because case height is often a determining factor in decisions about air transportation. If we apply similar calculations to a painting of 2000mm height the values of θ , the CTA, are 6.9° (50mm insulation), 8.8° (100mm), 9.3° (100mm on large faces). The last option improves CTA by 43% over the first.

Figure 2:

Section through a packing case with feet at its "Critical Toppling Angle"



So far we have considered a very rudimentary box transit case. One almost universal addition to this model is the provision of feet to raise the case clear of the ground and provide access for mechanical handling equipment. Because the mass of the feet is small in relation to the total mass of case and contents, we can assume that the centre of gravity remains at the intersection of the diagonals (Fig. 2). The CTA is derived from the expression

$$\tan \theta = a / (b + 2f)$$

where f is the height of the foot. Going back to our original 50mm thick insulation, the CTA of a transit case containing a 1000mm high painting with 100mm feet becomes 10.5° (86% of its former value). For a 2000mm high painting the transit case CTA is only 6° , 92% of the former value).

So far we have shown that adding insulation to transit cases for paintings significantly improves their stability and that feet markedly reduce stability. The obvious objection to added insulation is that the cases become larger and heavier. Simple calculations enable us to quantify these effects also.

Calculations of Volume and Weight

The volume of a case is equal to the product of its height, width and depth.

$$V = a \times b \times c$$

The weight of a case equals the weight of wood plus the weight of insulation. The weight of wood equals the density of wood multiplied by the volume of wood (the difference between the interior and exterior case volumes). Similarly, the weight of the insulation is found by multiplying the density of the insulation by the volume of the insulation (the difference between the interior case volume and the contents volume). The volume and net weight for the 3 case types examined above are tabulated below, the same 1000 x 1200 x 100 mm painting serving as the model. The densities of wood⁽³⁾ and polystyrene foam⁽⁴⁾ are taken as 0.5g/cm^3 and 20 kg/m^3 respectively.

TABLE 1

Type	Volume m^3	Net Weight kg
50mm insulation	0.39(100%)	53.5(100%)
100mm "	0.63(162%)	72.9(136%)
100/50mm "	0.59(151%)	68.3(128%)

(The % values in brackets are given to allow easy comparisons.)

Adding insulation causes significant increases in net transit case weights and volumes. The increases result result mainly from the effect of increased overall size on the wooden outer envelope rather than the insulation which contributes only about 10% of total net case weight. The example uses a rather lightweight wooden construction. For real cases with stiffening battens the relationships are more complex but still capable of calculation.

Comparing the Thermal Half-Time for Transit Cases

A simple equation for predicting the thermal half-time for a transit case is⁽⁵⁾

$$t_{\frac{1}{2}} = 0.693 (M s / U A)$$

where M is the mass of the contents
 s is the specific heat of the contents
 U is the thermal transmittance of the case
 A is the average of the surface area of the case and the surface area of the load or contents space

We can develop this equation⁽⁶⁾ for cases with differing thicknesses of insulation on different faces

$$t_{\frac{1}{2}} = 0.693 (M s / 2[U_1 A_1 + U_2 A_2 + U_3 A_3])$$

where A_1, A_2, A_3 are the average surface areas of the three different faces
 U_1, U_2, U_3 are the thermal transmittances of the three different walls

For a multilayer wall the thermal transmittance or "U value" is derived from the thicknesses (d_I, d_{II} etc.) and thermal conductivities (k_I, k_{II}) of the individual layers:

$$U_{\text{total}} = 1 / (d_I/k_I + d_{II}/k_{II} \text{ etc.})^{(7)}$$

Using values of thermal conductivity of 0.035 W/m² for polystyrene foam and 0.100 W/m² for wood (pine of intermediate moisture content)⁽⁸⁾ and taking the standard 50mm case as 100% (to eliminate the "Ms" term, the thermal capacity of the contents) the following relative half times were calculated:

TABLE 2

Type	Relative thermal half-time %
50mm insulation	100
100mm "	162
100/50mm "	140

Conclusions

Simple mathematics and basic physics allow us to predict the fundamentals of performance of variants of a standard packing case design. Even though this paper used a very straightforward case design the general approach could be applied to more complex "real life" designs provided they followed a consistent pattern. (Work is in progress at the Tate Gallery on a computer program that will carry out these calculations at the design stage so that the thermal half-time, net weight, volume and critical toppling angle will be known from the dimensions of the painting as an aid to decision-making concerning loans).

Much of the benefit of increased thermal half-time associated with higher standards of insulation is obtained with the intermediate design (100mm on large faces only) and this option is considerably less heavy and bulky than the full 100mm case. In addition, it offers the best depth/height ratio and therefore the highest critical toppling angle.

References

- (1) G.W.C.Kaye and T.H.Laby, Tables of Physical and Chemical Constants, Longmans, London, 12th edition 1959, pp.220-221
- (2) P.J.Wilson, "Temperature and Relative Humidity Control Strategies for Works of Art in Transit", Preprints of UKIC Mtg: "Safer Transport for Museum Objects", UKIC, London, 1985
- (3) Kaye and Laby, op. cit., p30
- (4) R.M.E.Diamant, Thermal and Acoustic Insulation, Butterworths, London, 1986, p144
- (5) P.J.Wilson, op. cit.
- (6) R.M.E.Diamant, op. cit., p8
- (7) ibid., pp.9-10
- (8) ibid., p144



Working Group 13

Natural History Collections

Collections d'histoire naturelle



SUMMARY

The oxidation of pyrite or marcasite, the dimorphs of ferrous disulphide, commonly causes the destruction of geological specimens. Conditions that favour high rates of oxidation include fine grain size of the reactive material, high relative humidity, and high temperature. The predominant oxidation products in specimens are sulphuric acid and hydrated ferrous sulphates. It is probable that the presence of oxidation products in specimens accelerates both specific oxidation rates and mechanical disintegration of specimens. Exposure of affected specimens to ammonia gas over a solution of a humectant and ammonium hydroxide has been shown to be effective in converting oxidation products to more humidity-stable compounds. This will certainly reduce damage to specimens from crystalline oxidation product hydration and dehydration reactions, but further experimental work is required to assess the effect of treatment on specific oxidation rates.

AN EXPERIMENTAL AMMONIA GAS TREATMENT METHOD FOR OXIDIZED PYRITIC MINERAL SPECIMENS

Robert Waller
Mineral Sciences Division
National Museum of Natural Sciences
National Museums of Canada
Ottawa, K1A 0M8, CANADA

INTRODUCTION

Pyrite is the cubic dimorph of ferrous disulphide. Marcasite is the orthorhombic dimorph of the same composition¹. Both fine grained pyrite and fine grained marcasite have been observed as being the affected material in mineral specimens undergoing oxidation. The oxidation products are the same in both cases. X-ray diffraction of the reacting material is the only certain way to distinguish which of the two phases is present. Although marcasite is considered the more reactive of the two forms, their chemical behavior is similar² and differences in surface area can lead to differences in oxidation rates comparable to the difference in rates between the dimorphs^{3,4}. Consequently, most information in this paper is applicable to specimens containing either reactive pyrite or reactive marcasite, hence in most instances pyrite can be read as pyrite and/or marcasite.

Decrepitation of oxidized pyritic mineral specimens is one of the most common types of damage that occurs in mineral specimen collections. While other types of damage often leave specimens that have some, albeit reduced, value, the damage that results from pyrite oxidation often leaves specimens in such a state that they are simply discarded. Because reactive pyrite may occur as an accessory mineral in specimens of many different mineral species, oxidation problems tend to be widespread throughout collections.

Pyrite in the presence of oxygen is thermodynamically unstable with respect to a variety of iron and sulphur bearing compounds. At moderate temperatures pyrite oxidizes according to the reaction^{5,6}: $\text{FeS}_2 + 3\text{O}_2 \rightarrow \text{FeSO}_4 + \text{SO}_2$. It should be noted that the oxidation is of sulphur⁴ and not of iron. An x-ray photoelectron spectroscopy study has shown that this or a similar reaction occurs virtually instantly when freshly fractured pyrite surfaces are exposed to air⁷. In the absence of moisture the sulphate coating appears to passivate the remaining pyrite.

In the presence of moisture the predominant overall reaction is^{5,8}: $2\text{FeS}_2 + 7\text{O}_2 + n+m+2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 \cdot n\text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 \cdot m\text{H}_2\text{O}$. Both oxidation products are hydrated. The sulphuric acid is in solution with water. The concentration of the solution varies as a continuous function of relative humidity. The ferrous sulphate is present both as crystalline hydrates and in solution. The hydrate phases commonly observed are $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite), $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite) and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (szmolnikite).

Clearly, the disulphide to sulphate reaction which involves seven electrons per sulphur cannot occur as a single step but since intermediate valence products are not commonly observed and the stoichiometry indicated in the equation has been demonstrated^{5,8} it can be assumed that the rate of oxidation of intermediate products is rapid in comparison to an earlier rate limiting step.

Ferrous sulphate is subject to further oxidation and hydrolysis leading to a variety of ferrous-ferric-sulphate-hydroxide-hydrate phases. In addition the acidic sulphate solution frequently attacks associated mineral species resulting in the formation of sulphates with a variety of cations or cation mixtures. Anglesite (PbSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), halotrichite ($\text{FeAl}_3(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), and copiapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) are just a few of the diverse species that may appear as decomposition products. In spite of the great variety of possible end-products, ferrous sulphate and sulphuric acid are generally the predominant oxidation products found on specimens in collections.

Mineral specimens are almost always stored at relative humidities less than 100%. Consequently, oxidation occurs in undersaturated conditions. Sulphide oxidation reactions in saturated systems have been studied extensively but are still far from being completely understood. Reactions in undersaturated conditions, in contrast, have received little attention.

It is helpful to realize however, that the importance of water is as a medium in which the oxidation occurs more than as a reactant

itself. Even if electrochemical reactions involving dissociation of water are occurring, the necessity of the presence of bulk water as a medium overwhelms any significance of the concentration of water as a reactant. In support of this, North and Smith⁹ found that reaction rate data for undersaturated conditions, when extrapolated to 100% RH, agreed well with rate data for in vitro oxidation. Consequently, appropriate data from experiments in saturated systems are useful for describing behaviour in undersaturated systems.

For example, temperature, pH and oxygen concentration dependence of reaction rates are applicable to undersaturated conditions provided they were applicable to saturated, high pulp density, and high ionic strength conditions.

The activation energy for aqueous oxidation of pyrite by oxygen over the range 20-40°C, according to a recent investigation¹⁰, is $56.9 \pm 7.5 \text{ kJ} \cdot \text{mol}^{-1}$. This differs from the value of $39 \text{ kJ} \cdot \text{mol}^{-1}$ reported by Mathews and Robins¹¹ but agrees well with the findings of North and Smith⁹ who reported a value of $59 \text{ kJ} \cdot \text{mol}^{-1}$ over the temperature range 20-35°C. Assuming $60 \text{ kJ} \cdot \text{mol}^{-1}$ is close to the correct value, then near room temperature, when all other factors are equal, oxidation rates will approximately double for every 10°C rise in temperature.

Several investigators^{8,10,11} have found that there is little or no dependency of oxidation rate on pH over the range $-1 < \text{pH} < 4$. The pH in actively oxidizing pyritic areas in specimens will be within this range. At higher pH, oxidation rates increase as a function of pH.

Little data is available on the dependence of oxidation rate on relative humidity. North and Smith⁹ found the rate of oxidation to monotonically increase with increasing relative humidity over the RH range 31 to 96% within the temperature range 25 to 45°C. Their data can be plotted in the form of the empirical, exponential function employed by Rice et al.¹² to describe the RH dependence of metallic oxidation rates: $r = A \exp(b \text{ RH})$. In this equation the factor b found for a material reflects the sensitivity of that material's corrosion to relative humidity. The data from North and Smith for pyrite oxidation at 25°C gave an RH dependency factor (b) of 2.67. This indicates a relatively low dependence compared with metals in polluted atmospheres, for example, copper (b=4.6) and iron (b=12.6)¹². Using this equation and 2.67 as the RH dependency factor it can be calculated that the oxidation rate will double for every 26% increase in RH.

HISTORY OF CONSERVATION METHODS

Howie¹⁴ reviewed conservation treatments for oxidized pyritic specimens that appeared in the literature between 1842 and 1976. The earliest conservation methods involved isolating specimens from the atmosphere using fluids such as linseed oil. In 1908 Bather¹⁵ suggested that where immersion is not suitable for a specimen, that neutralization in a hot solution of caustic alkali followed by drying in a solution of alcohol or petrol and consolidation with shellac or paraffin would prolong specimen life.

In 1929, Radley¹⁶ published the results of an impressive ten year study of the oxidation of pyritic specimens. His findings included: that fine grained disseminated pyrite was susceptible to rapid oxidation while coarsely crystalline material was relatively stable; that sodium chloride contamination led to the formation of the very deliquescent ferrous chloride which greatly accelerated oxidation, and that removal of oxidation products was an essential step in a conservation treatment. He recommended thorough washing and drying of specimens followed by consolidation with dope (cellulose nitrate) as the best method of treatment.

Bannister¹⁸ in 1933 and Bannister and Sweet¹⁹ in 1943 recommended as a conservation treatment that specimens be exposed to the vapours of a concentrated ammonium hydroxide solution prior to consolidation with polyvinyl acetate. This treatment, with modification of the consolidant used, has been the most common treatment employed for the conservation of oxidized, pyritic specimens^{20,21,22}.

Gordon¹⁷ in 1947 pointed to the hygroscopic nature of ferrous sulphate oxidation products and suggested that hydration pressures developed in the oxidation products are responsible for the disintegration of specimens. For treatment, he recommended extraction of the ferrous sulphate oxidation product in concentrated hydrochloric acid. Other solutions that have been

recommended for the extraction and/or neutralization of oxidation products²⁰ include: aqueous ammonium hydroxide¹⁸, ammonia²⁴ in alcohol²⁰, morpholine in alcohol²⁰, aqueous sodium bicarbonate²⁴, ammonium thioglycollate in alcohol¹³, ethanolamine thioglycollate in alcohol²³ as well as a number of disinfectant solutions.

Booth and Sefton²⁵ recommended the use of 4-chloro-m-cresol, an effective vapour phase inhibitor for thiobacteria, as a vapour phase inhibitor of pyrite oxidation. It has, however, been found to be ineffective²⁶.

RATIONALE FOR CONSERVATION TREATMENT

While nearly all authors recommending treatment methods for oxidized pyritic specimens recommend removal and/or neutralization of oxidation products^{18,19,20,21,22,23}, only Radley and Gordon have suggested reasons why this removal is necessary. Radley suggested that deliquescent substances among the oxidation products enhance oxidation rates and Gordon suggested that expansion resulting from hydration of the ferrous sulphate oxidation product contributes greatly to specimen decrepitation. It is likely that they are both correct.

Sulphuric acid has an extremely low vapour pressure at room temperature and hence can not be expected to evaporate away from specimens. It is, however, highly reactive and most of what is produced during the oxidation of pyrite will be consumed in reactions with associated minerals. Still, the sites at which the sulphuric acid is consumed are often separated some millimeters from the sites at which the acid is being produced. Consequently, even if production of sulphuric acid were arrested completely, some acid would remain indefinitely on the pyrite surfaces (pyrite itself does not undergo nonoxidative dissolution in sulphuric acid²⁷).

Sulphuric acid is deliquescent at all levels of relative humidity (Figure 1). As a result, it exists as a strong electrolyte solution when in equilibrium with any level of relative humidity. It will both serve as a solvent for removing otherwise passive oxide coatings and act as an electrolyte to support any electrochemical oxidation that might occur.

Ferrous sulphate, at room temperature, will exist as any of three hydrates as described above. The substitution of other divalent cations for iron in this mineral will lead to changes in both which hydrates form²⁸ and the equilibrium vapour pressure for a given hydrate pair. Still, data for pure ferrous sulphate is representative of the sort of hydration reactions that occur. At about 50% RH the one to four hydrate transition occurs resulting in a molar volume expansion of 73%. At about 60% RH the four to seven hydrate transition occurs resulting in a 48% molar volume expansion (Figure 2). The destructive effects on rock of salt hydration are well known and even form the basis of a standard test for rock soundness (ASTM C 88-83).

Apparently, both of the major oxidation products are not inert and will accelerate specimen deterioration, even at moderate levels of relative humidity. It is for this reason that treatments which either remove or stabilize oxidation products are thought to be an essential part of a conservation treatment.

AMMONIA GAS TREATMENT

Limiting the applicability of any method involving immersion of specimens is the fact that many specimens which have undergone oxidation to a significant extent are so friable that they completely disintegrate on wetting. The practice of exposing specimens to the vapours of aqueous ammonium hydroxide is only a slight improvement over total immersion since condensation, aided by deliquescence of oxidation and reaction products, occurs in fractures in the specimen. In most cases this causes specimen disintegration just as total immersion in a fluid would. Dry ammonia gas has been used experimentally¹³, but its safe use requires expensive, specialized equipment.

By adding a humectant to a solution of ammonium hydroxide it is possible to obtain a solution that provides a source of ammonia gas while depressing the water vapour pressure to a level at which condensation will not occur in fractures. The level to which water vapour pressure is depressed was selected somewhat arbitrarily to be equivalent to about 50% RH. The level must be lower than 80% RH which is the deliquescence point of $(\text{NH}_4)_2\text{SO}_4$ and it was thought

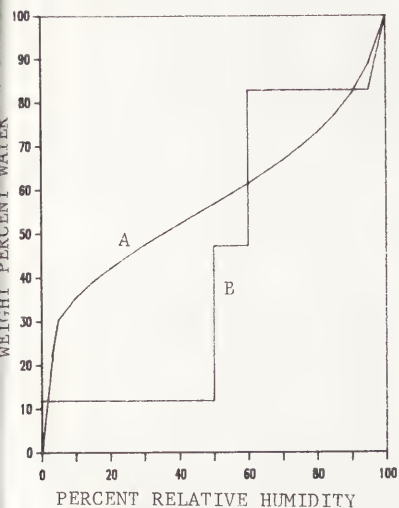


Figure 1. Weight percent water as a function of relative humidity for A) sulphuric acid and B) ferrous sulphate. Based on data from refs. 30, 31 and 33.

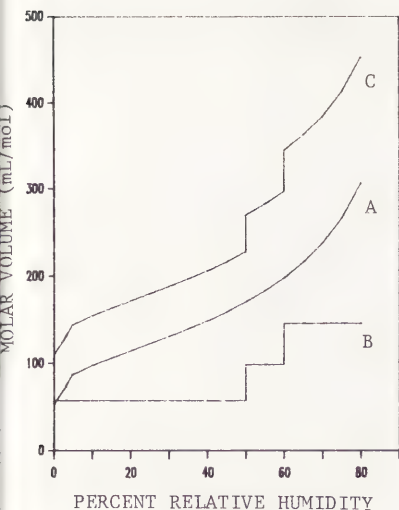


Figure 2. Molar volumes of A) sulphuric acid; B) ferrous sulphate; and C) an equal mixture of both. Curve C has been drawn assuming no interaction occurs between the two substances and that the ferrous sulphate does not contain significant amounts of other ions in solid solution. From data in refs. 30, 31 and 33.

that it should be kept below 60% RH which is the level that Howie found the greatest increase in the rate of increase of water absorption as a function of relative humidity¹³.

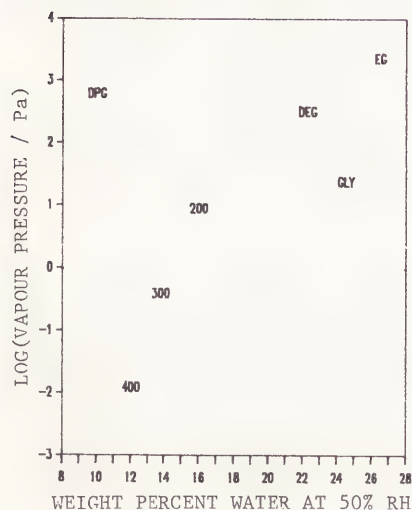


Figure 3. Comparison of hygroscopicity (g(water)/100 g(dry humectant)) and vapour pressure (at 100°C) for some common humectants. DEG = diethylene glycol DPG = dipropylene glycol EG = ethylene glycol GLY = glycerol 200 = PEG 200; 300 = PEG 300 400 = PEG 400 Data from refs. 29 and 30.

Hygroscopic organic liquids such as glycerol and the various glycols were considered for use as humectants. The characteristics of the ideal humectant for this application include: high hygroscopicity, low vapour pressure, ready availability, low cost, and low viscosity. Of these characteristics it is high hygroscopicity and low vapour pressure which are most important. Certain of these properties are interrelated. Most significantly hygroscopicity tends to decrease with decreasing vapour pressure (Figure 3). Considering the great importance of low vapour pressure for minimizing contamination of specimens by the humectant, polyethylene glycol 400 (PEG 400) was chosen over glycerol and the lower average molecular weight glycols all of which exhibit greater hygroscopicity.

The water content of a PEG 400 solution that exerts a water vapour pressure equivalent to 50% RH is 0.12 g_{water}/g_{PEG 400}. Standard concentrated NH₄OH contains 0.65 kg_L⁻¹ of water. Assuming that the dissolved NH₃ will not greatly affect the equilibrium relative humidity (ERH) of a PEG 400-NH₃-H₂O solution it is apparent that a solution of 0.2 mL of concentrated NH₄OH in 1 g of PEG 400 will possess an ERH of ~50%.

The assumption that the ERH of the solution is not greatly affected by the NH₃ present was found to be valid when granular samples of a series of deliquescent salts were placed into a treatment cabinet over a 0.2 mL g⁻¹ solution NH₄OH in PEG 400. Potassium carbonate, deliquescent at or above 43% RH, dissolved extensively while magnesium nitrate, deliquescent at or above 55% RH showed only slight welding of the grains, probably due to capillary co-condensation of NH₃ and H₂O.

The duration of treatment required for a particular specimen is generally not known. This time will depend not only on gross specimen size but will be influenced by the concentration and distribution of decomposition products, the permeability of the specimen (primarily through fractures), the ratio of the amount of oxidation products to the amount of ammonia available in the reservoir, and the extent to which ammonia is lost by escape from the treatment container. The only sure method of knowing that a specimen has reacted through to its core is to break it apart. This is clearly not acceptable for non-test specimens.

It is possible, however, to provide an indication of the probable depth of reaction in a specimen and, at very least, a record of the extent of treatment. This can be done by including in the reaction container a glass tube containing a fixed amount of reactive sulphate in an inert granular dilutant. Ferrous sulphate would be the obvious source of reactive sulphate to employ but to try to obtain a sharp, readily apparent colour distinction between reacted and non-reacted material several sulphates were tested. Of those tested (FeSO₄·nH₂O, CuSO₄·5H₂O, CoSO₄·nH₂O, Fe₂(SO₄)₃·nH₂O) ferric sulphate showed the clearest colour contrast between reacted and non-reacted material. Various quantities of ferric sulphate mixed with -200,+325 mesh glass beads were placed in 4 mm ID glass tubing sealed at one end. Similar tubes were prepared using a sample of the most severely oxidized specimen available (NMNS 52668) formerly catalogued as a pyritized slickenside but currently a mixture of powdery sulphates, primarily ferrous sulphate, and fine granular material, largely quartz and euhedral pyrite. One of the tubes prepared from this specimen was made up from material ground to -200 mesh to, in part, make up for the loss of compaction that the specimen material undergoes on being transferred to a tube.

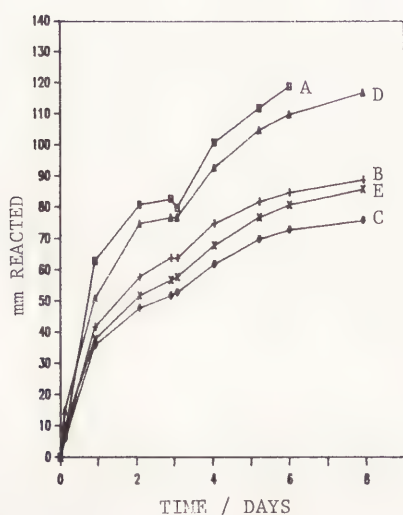


Figure 4. Extent of reaction as a function of time for 4 mm ID glass tubes filled with A) 0.5 mol(sulphate) kg⁻¹; B) 1.0 mol(sulphate) kg⁻¹; C) 1.5 mol(sulphate) kg⁻¹; D) NMNS #52668; and E) -200 mesh ground sample of NMNS #52668 on exposure to NH₃-H₂O-PEG 400 solution as described in the text. Note the effect of replenishing the solution on day three.

Series of these tubes were supported vertically, open end up, in a treatment container. The concentration of ferric sulphate in glass beads that showed a reaction rate nearest that of the -200 mesh specimen material was 1.0 mol(SO₄²⁻)·kg⁻¹ (Figure 4). This mixture gently tamped into a 4 mm ID glass tube has been adopted as a standard and included with specimens in treatment containers for recording extent of treatment and estimating the required duration of treatment. It should be noted that since Fe₂(SO₄)₃·nH₂O has a variable water content it is essential that the water of hydration be determined and accounted for when a mixture is prepared.

Assuming that specimens to be treated are isotropic and react at least as quickly as the standard tube then the specimen will be completely reacted when the tube has reacted to a depth equal to one half of the minimum box dimension of the specimen. In practice, to provide a margin for uncertainty, specimens are

treated until the tube has reacted to a depth approximately equal to the minimum box dimension of the specimen.

A variety of severely oxidized test specimens treated to this extent have been broken apart and pressed against filter paper dampened with a solution of the indicator bromocresol green (blue to yellow colour change at pH 5.4-3.8). These have all shown complete conversion of acid and hydrolyzable sulphates during treatment when the duration of treatment was such that the indicating tube reacted to a depth approximately equal to the minimum box dimension of the specimen.

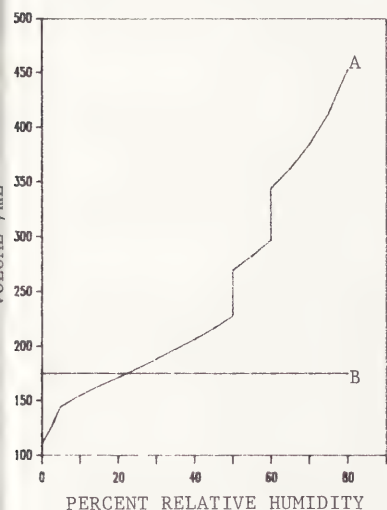
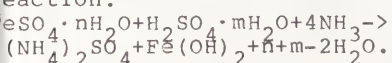


Figure 5. Comparison of the calculated volumes of the solid reactants (A) and the solid products (B) in the reaction:



A possible cause of concern when reacting a specimen with a gas is possible damage due to expansion occurring during the reaction. This treatment may or may not result in such expansion. The volume occupied by given molar quantity of decomposition products is highly dependent on the relative humidity to which the products have equilibrated. Figure 5 compares the volume of one mole of each of the oxidation products, ferrous sulphate and sulphuric acid, with an equivalent amount of the reaction products, ammonium sulphate and ferrous hydroxide, over the relative humidity range 0-80%. The assumptions made for Figure 2 also apply to Figure 5. It is also assumed that the volume occupied is proportional to the molar volume for both reactants and products, that is that crystal morphology and orientation preferences do not result in much less than complete infilling. None of these assumptions are completely valid. Still, this information does illustrate the trends for molar volume as a function of RH. It can be seen that where oxidation products have equilibrated with an atmosphere having a relative humidity of 20% or higher there will be a reduction of molar volume on reaction with ammonia. Most importantly, Figure 5 shows that the oxidation products which are hygroscopic over the entire RH range will be rendered non-hygroscopic over the range 0-80% RH.

PROCEDURE

Specimens are placed on an open mesh or grid support in a container preferably a desiccating cabinet. If very large specimens have to be treated the container could simply be a large plastic bag. A laminated plastic with low permeability polyvinylidene chloride layer would be preferred. If only certain areas of a very large specimen need to be treated then it may be possible to use a tent of plastic as the container. One of the standard ferric sulphate and glass bead mixture tubes is attached to a ruler or similar graduated scale is placed in the container in a easily viewed position. Deviation of the tube from a vertical position does not affect the rate of reaction but the open end should be placed at the same level in the container as the specimen. Daily readings of the position of the reaction front along the tube will reveal when the ammonia has been depleted.

Several hundred grams of PEG 400 are weighed into a shallow tray, preferably a stainless steel tray. 0.2 mL conc. NH_4OH per g PEG 400 is added to this and stirred quickly and thoroughly then the tray is placed into the container, preferably beneath the specimen.

When the reaction front in the tube is no longer advancing from day to day then the supply of ammonia must be replenished. The water must be removed from the PEG before it can be reused. This can be done by heating the solution in its pan to about 150°C. If the solution is stirred while it is being heated it will be noticed that streams of bubbles form as long as water is present but cease to form when it has been driven off. This simple test need only be performed the first time a solution must be dried provided the time required is recorded. Thereafter, if the same heater, pan and solution volume are used, heat can simply be applied for the pre-determined time plus about ten percent to allow for variations in mains voltage.

Polyethylene glycols will slowly break down at elevated temperatures to give products having higher vapour pressures than the original polymer³². Hence, it is advisable to discard the solution after it has been recycled three or four times or when it is no longer perfectly clear and colourless.

The treatment is considered complete when the indicating tube has reacted to a depth approximately equal to the minimum box dimension of the specimen. The exact depth of reaction in the indicating tube is recorded as part of the conservation treatment record. The specimen is then placed in a dry (<50%RH) well aerated area for several days to allow residual ammonia in the specimen to

dissipate. After ammonia gas treatment specimens typically require both consolidation and removal of surficial reaction products.

It is unrealistic to expect the consolidant to provide protection from the ingress of oxygen and water vapour both because consolidants are permeable to these gasses and because complete and perfect sealing of all open paths for such ingress is virtually unachievable. It is also unreasonable to try to achieve a strength of consolidation that would withstand the pressure of renewed oxidation product formation and hydration. Hence, the objective of consolidation is only to strengthen the specimen to withstand normal handling and vibration. Long-term reversibility is not a consideration for most specimens as they would be destroyed by immersion in any solvent.

Consequently, the selection criteria for a consolidant are excellent long-term stability, short-term reversibility and ease of application. Thermoplastics applied in solution in organic solvents are considered suitable. In particular, "Butvar B98" (polyvinyl butyral) and "Acryloid B72" (ethyl methacrylate/methyl acrylate copolymer) have been used with no apparent problems for at least three years following treatment.

The solvent used with the consolidant could be selected on the basis of both concentration-viscosity ratio and vapour pressure. As data was not available for the former, selection was made on the basis of the latter. A high vapour pressure, and hence evaporation rate, allows the consolidant solution to dry almost completely within twenty four hours facilitating daily repeated injections. Water vapour condensation due to evaporative cooling of the solvent was not considered to be a problem due to the generally small width of fractures which precludes air/vapour convection and results in a small overall rate of evaporation in comparison to the heat capacity of specimens. Consequently, acetone (vapour pressure 25 kPa at 20 °C³¹) and tetrahydrofuran (vapour pressure 17 kPa at 20 °C³¹) were chosen as the solvents for the "Acryloid B72" and "Butvar B98" respectively. Consolidation is performed as repeated injections into fracture networks using a syringe and small gauge needle.

Removal of reaction products from exposed surfaces is done with an "SS White" air abrasive machine using -80 mesh granulated cork as the media and an operating pressure of about 0.2 MPa (gauge).

Following treatment specimens must be kept at as low a relative humidity as possible. A lower limit to the RH level may be dictated by requirements of associated minerals³³ but most often it is possible to store specimens over a desiccant. Depending on the number and sizes of problem specimens this can be achieved by using individual jars or similar containers or by using large quantities of desiccant in carefully sealed cabinets.

DISCUSSION

Specimens treated by this method have shown no change in condition for up to four years. It is also comforting to note that experience in other museums²⁰ has also indicated that ammonia based treatments are effective in retarding specimen deterioration. Still, observation for a decade or less of the behaviour of treated and untreated specimens is probably not a reliable indicator of the long-term suitability of a treatment method. This is especially true since specimens are generally stored at a lower relative humidity after treatment than they were stored at before treatment. By reducing the relative humidity around a specimen both the molar volume of oxidation products and the rate at which oxidation products are produced will be reduced. These two factors taken together should by themselves make specimens appear stable for several years or decades.

Ammonia gas neutralization will certainly be effective in eliminating the development of hydration pressure in oxidation products. Whether it reduces, has no effect, or actually increases specific pyrite oxidation rates can only be answered by measurements of such rates both before and after treatment. Measurements of specific pyrite oxidation rates as a function of relative humidity, temperature, time and sample pretreatment are planned and will be reported at the next triennial meeting.

In the meantime, it is recommended that this treatment be reserved for those specimens that, through careful documentation, have been shown to be continuing to deteriorate in spite of being stored in the best (coolest and lowest relative humidity) climate possible. The treatment, being experimental, should in fact be reserved for

specimens that would otherwise be discarded. Above all, it must be remembered that no treatment for oxidized pyritic specimens that has yet been proposed will, in any way, obviate the need for climate control for ongoing preservation.

ACKNOWLEDGEMENTS

I would like to thank Fred Hartwick, National Museum of Natural Sciences for technical assistance, and Joel Grice, National Museum of Natural Sciences, and Ian Wainwright, Canadian Conservation Institute, for reviewing the manuscript.

REFERENCES

- 1 Deer, W.A., Howie, R.A. and Zussman, J. (1962) *Rock-forming Minerals*, Volume 5, Non-silicates. Longmans, London.
- 2 Allen, E.T., Crenshaw, J.L., Johnston, J. and Larsen, E.S. (1912) "The mineral sulphides of iron", *American Journal of Science*, Fourth Series, **33**, 169-236.
- 3 Caruccio, F.T. (1975) "Estimating the acid potential of coal mine refuse", *British Ecological Society, Symposium*, **15**, 197-205.
- 4 Pugh, C.E., Hossner, L.R. and Dixon, J.B. (1984) "Oxidation rate of iron sulfides as affected by surface area, morphology, oxygen concentration, and autotrophic bacteria", *Soil Science*, **137**(5), 309-314.
- 5 Braley, S.A. (1954) "Summary Report on Commonwealth of Pennsylvania Department of Health Industrial Fellowship Nos. 1,2,3,4,5,6,7", Mellon Institute of Research, Pittsburgh.
- 6 Banerjee, A.C. (1971) "Mechanism of oxidation of iron pyrites", *Chemical Society of London. Journal. Chemical Communications*, 1006-1007.
- 7 Clifford, R.K., Purdy, K.L. and Miller, J.D. (1975) "Characterization of sulphide mineral surfaces in froth floatation systems using electron spectroscopy for chemical analysis", *American Institute of Chemical Engineers. Symposium Series*, **71**(150), 138-147.
- 8 Smith, E.E. and Shumate, K.S. (1970) "Sulfide to sulfate reaction mechanism", *Water Pollution Control Research Series, Report 14010 FPS02/70*, US Department of the Interior.
- 9 Morth, A.H. and Smith, E.E. (1966) "Kinetics of the sulfide-to-sulfate reaction", *American Chemical Society Division of Fuel Chemistry*, **10**(1), 83-92.
- 10 McKibben, M.A. and Barnes, H.L. (1980) "Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures", *Geochimica et Cosmochimica Acta*, **50**, 1509-1520.
- 11 Mathews, C.T. and Robbins, R.G. (1974) "Aqueous oxidation of iron disulphide by molecular oxygen", *Australian Chemical Engineering*, **15**, 19-24.
- 12 Rice, D.W., Cappell, R.J., Kinsolving, W. and Laskowski, J.J. (1980) "Indoor corrosion of metals", *Journal of the Electrochemical Society*, **127**(4), 891-901.
- 13 Howie, F.M.P. (1979) "Museum climatology and the conservation of palaeontological material", *Special Papers in Palaeontology*, **22**, 103-125.
- 14 Howie, F.M.P. (1977) "Pyrite and conservation", *Newsletter of the Geological Curator's Group*, **1**, 457-465, 497-512.
- 15 Bather, F.A. (1908) "The preparation and preservation of fossils", *Museums Journal*, **8**(3), 76-90.
- 16 Radley, E.G. (1929) "The decomposition of pyritized and other fossils", *The Naturalist*, April 143-146, May 167-173, June 196-202.
- 17 Gordon, S.G. (1947) "Preservation of specimens of marcasite and pyrite", *American Mineralogist*, **32**, 589.
- 18 Bannister, F.A. (1933) "The preservation pyrites and marcasite", *Museums Journal*, **33**, 72-75.
- 19 Bannister, F.A. and Sweet, J.M. (1943) "The decomposition of pyrite", *Museums Journal*, **33**, p8.
- 20 Rixon, A.E. (1976) *Fossil Animal Remains: Their Preparation and Conservation*. The Athlone Press, London.
- 21 Plenderleith, H.J. (1956) *The Conservation of Antiquities and Works of Art*. Oxford University Press, London.
- 22 Oddy, W.A. (1977) "The conservation of pyritic stone antiquities", *Studies in Conservation*, **22**, 68-72.
- 23 Cornish, L. and Doyle, A. (1984) "Use of ethanolamine thioglycollate in the conservation of pyritized fossils", *Palaeontology*, **27**(2), 421-424.
- 24 Hansen, G.R. (1979) "Preserving pyrite", *Mineralogical Record*, **10**(1), 56.
- 25 Booth, G.H. and Sefton, G.V. (1970) "Vapour phase inhibition of thiobacilli and ferrobacilli: a potential preservative

- for pyritic museum specimens", *Nature*, **226**, 185-186.
- 26 Howie, F. (1978) "Storage environment and the conservation of geological material", *The Conservator*, **2**, 13-19.
- 27 Lowson, R.T. (1982) "Aqueous oxidation of pyrite by molecular oxygen", *Chemical Reviews*, **82**(5), 461-497.
- 28 Jambor, J.L. and Traill, R.J. (1963) "On rozenite and siderotil", *Canadian Mineralogist*, **7**(5), 751-763.
- 29 Carbowax[®] Polyethylene Glycols. (1966) and Glycols. (1955) Union Carbide Corporation, Old Ridgeway Road, Danbury, CT.
- 30 Weast, R.C., ed. (1976) *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, Cleveland.
- 31 Dean, J.A., ed. (1979) *Lange's Handbook of Chemistry*, McGraw-Hill Book Company, New York.
- 32 Brownstein, A.D. (1982) "The chemistry of polyethylene glycol", in: Grattan, D.W. with McCawley, J.C. (eds.) *Proceedings of the ICOM Waterlogged Wood Working Group Conference*, Ottawa, 1981.
- 33 Waller, R. "Temperature and humidity sensitive mineralogical and petrological specimens", in Howie, F. (ed.) *Conservation of Geological Specimens*, in preparation.

Working Group 14

Graphic and Photographic Documents

Documents graphiques et
photographiques



MEMBRES :

D.P. AGRAWAL (Inde)
 J.-M. ARNOULT (France)
 G. BANIK (Autriche)
 S. BARGER (U.S.A.)
 M.G. BLANK (U.R.S.S.)
 E. BOYD (United Kingdom)
 H. BURGESS (Canada)
 A. CARTIER-BRESSON (France)
 S. FLETCHER (U.S.A.)
 B. GUINEAU (France)
 J. HOFENK de GRAAF (Pays-Bas)
 A. KING (U.S.A.)
 J.E. KLINGER (U.S.A.)
 M. S. KOCH (Danemark)
 M. KORT (Pays-Bas)
 Ju P. NYUKSHA (U.R.S.S.)
 J. REILLY (U.S.A.)
 S. REMPEL (U.S.A.)
 W. ROELOFS (Pays-Bas)
 R. ROSE (U.S.A.)
 J. STONE (U.S.A.)
 F. VITALE (U.S.A.)
 M.V. YUSUPOVA (U.R.S.S.)
 M. ZAPPALA (Italie)

Coordinateur :
 Françoise FLIEDER (France)

Coordinateur-adjoint
 Klaus HENDRIKS (Canada)

Les activités de notre groupe se sont notablement développées durant ces trois dernières années grâce à l'organisation d'un colloque et à la création d'un bulletin de liaison.

En effet, afin de faire le point sur l'état d'avancement du programme de travail établi à Copenhague, une réunion restreinte s'est tenue à Paris les 22 et 23 avril 1986. Une trentaine de personnes y assistaient, onze communications ont été présentées.

La première journée était consacrée aux exposés des travaux sur la conservation des papiers et des matériaux photographiques ainsi qu'aux problèmes posés par l'analyse des pigments des manuscrits. M. ARNOULT a traité de la désacidification de masse tandis que Mmes LECLERC et STONE abordaient la restauration des papiers transparents. Mme LECLERC nous a également parlé du comportement vis-à-vis de la pollution des papiers désacidifiés par différentes méthodes. Mme ZAPPALA a résumé son travail sur l'influence du plomb sur la conservation des papiers. M. GUINEAU a décrit les résultats qu'il a obtenus par spectrométrie Raman sur l'analyse de deux composés essentiels de la garance : l'alizarine et la purpurine. Mlle ROELOFS a plus particulièrement orienté sa communication sur les méthodes d'analyse des colorants et pigments organiques.

Durant la deuxième journée, les participants ont pu visiter les différents ateliers de restauration de la Bibliothèque Nationale et des Archives Nationales, ainsi que l'Atelier de restauration de photographie de la Ville de Paris et le Service des Archives Photographiques.

Par ailleurs, nous avons pu pour la première fois éditer un bulletin qui a permis d'améliorer considérablement la diffusion des informations. Le premier numéro est sorti en janvier 1985, il a été suivi par deux autres, le prochain paraîtra en juin 1987.

Ce bulletin est composé de plusieurs rubriques, entre autres des notes techniques volontairement concises destinées aux praticiens de la restauration, une revue bibliographique analytique comportant notamment des comptes rendus des principaux congrès internationaux et un calendrier des manifestations à venir.

D'autre part, plusieurs membres du groupe ont participé à la réalisation d'un poster devant être présenté lors de la conférence générale de I.L.C.O.M. tenue à Buenos Aires en octobre 1986. Ce panneau illustre des travaux sur le colmatage de lacunes de papiers détériorés, sur la conservation au National Maritime Museum de Londres de papiers transparents du 19^e siècle, ainsi que sur la restauration de négatifs sur plaque de verre au gélatino bromure d'argent.

En outre, une collaboration s'est établie entre notre groupe et deux organismes internationaux préoccupés par les mêmes problèmes. Il s'agit du Comité de Conservation du Conseil International des Archives (C.I.A.) et du Comité de Conservation de la Fédération Internationale des Associations de Bibliothécaires (I.F.L.A.).

Enfin, l'essentiel de l'activité de notre groupe s'est traduit évidemment par le nombre important de communications présentées ici.

Celles concernant les **Documents Graphiques** portent sur l'évolution des techniques de restauration et de conservation utilisées à travers le monde, ainsi que sur les nouvelles recherches menées sur l'analyse des papiers, des parchemins et des pigments des manuscrits ornés. Certains travaux, en particulier ceux de Mmes LECLERC, STONE et BOYD et ceux de Mlle ROELOFS et M. GUINEAU, ont été réalisés en collaboration.

L'accent a été mis cette année sur les problèmes posés par la restauration. Le colmatage des lacunes a fait l'objet de deux études, la première est consacrée au parchemin et la deuxième au papier. Une méthode intéressante sur la restauration des papiers transparents est décrite ainsi qu'un travail original sur le traitement des papiers peints de grand format. Enfin, la poursuite des recherches faites sur la restauration des manuscrits sur feuilles de palmier et écorces de bouleau a abouti à des résultats très précieux pour toute personne préoccupée par la conservation de ces matériaux.

Dans le domaine de la conservation, l'étude de l'influence du plomb sur le comportement à long terme du papier apporte des éléments nouveaux. Une recherche sur le pouvoir antifongique du polyéthylène utilisé pour la lamination du papier a été réalisée. Deux communications traitent de la normalisation des essais pour les papiers, l'une décrit les différents critères de référence pour estimer la stabilité du matériau, l'autre est orientée sur le choix de "standards" pouvant définir un papier permanent.

Enfin de nombreuses techniques d'analyses (spectroscopie, micrographie, diffraction X, chromatographie et électrophorèse) sont utilisées pour mettre en évidence les produits de dégradation des papiers et des parchemins détériorés et pour identifier les pigments et les colorants organiques naturels tels que la garance. Des résultats très spectaculaires ont été obtenus sur des microéchantillons prélevés sur des manuscrits.

Pour les **Documents Photographiques**, les recherches ont porté sur l'identification des différents procédés anciens et sur la mise en évidence des traitements de restauration antérieurs. Le problème de l'intensification des clichés gélatino-argentiques pâlis a également été abordé.



SUMMARY

Some aspects of the problem of conservation of birch bark were studied earlier. This paper presents the results of further studies. The effect of various cleaning agents and bleaching agents was studied. The study of the effect of various adhesives on birch bark was also undertaken.

FURTHER STUDIES ON THE PROBLEMS OF CONSERVATION OF BIRCH BARK

O.P. Agrawal and D.G. Suryawanshi
National Research Laboratory for Conservation of Cultural Property
E/3, Aliganj Scheme, Lucknow - 226020 India

INTRODUCTION

Some studies on the problems of birch bark conservation were done in our Laboratory earlier [1]. As far as birch bark is concerned, it is considered necessary to know the effect of various chemicals on the strength and appearance of birch bark. With that aim in mind, the effect of various cleaning agents normally used in conservation was seen on it. It was also considered of interest to see the effect of bleaching agents on birch bark. The aim was to find out whether bleaching agents could be used for birch bark and if so, which will be the best.

Another important problem is of the use of adhesives. We were not sure which adhesive would work for repair of birch bark. With these aims in mind, the present studies were undertaken.

PART - I

STUDIES ON THE EFFECT OF CLEANING AGENTS ON BIRCH BARK

Water, various organic solvents and mixtures of chemicals were tried as cleaning agents. Bark samples of a general size 2.5 cm^2 were prepared for the treatment. Experiments were conducted by dipping the bark samples in solutions of cleaning agents at least for 2 hours at room temperature.

Observations were made on the changes in the appearance as well as the physical strength and the tendency for the separation of the various layers of bark samples. It may be recalled that birch bark has several layers sticking together by natural adhesive.

Effect of Water

The effect of water, direct from tap as well as distilled, cold or hot, was observed. The measurement of pH, brightness of the birch bark as well as its tendency for separation were noted. pH was measured by pH meter and brightness with the help of Brightness Meter.

Organic Solvents

The effect of acetone, ethyl alcohol, ether, carbon tetrachloride, trichloroethylene and xylene was observed. In addition, the effect of mixtures of some of the solvents was also seen. Results are given in Table-I.

It is found that many of the organic chemicals leach out some of the natural organic components of birch bark, resulting in the separation of thin layers of bark from each other. It is also observed that there is a considerable change in the colour of the bark by some of the above solvents. According to our observations, carbon tetrachloride, trichloroethylene and xylene are the most suitable for general cleaning. These particular chemicals did not show any immediate effect on the bark, either by dissolving natural constituents or in separating the layers of the birch. There was no shrinkage or any appreciable change in the appearance.

In the case of xylene particularly, it was observed that the original property and the physical strength of the bark did not change at all. The appearance and the colour of the bark also remained the same.

Effect of mixtures of chemicals

Several mixtures of chemicals were also tried for cleaning. The results and observations are as follows:

a) Ethyl alcohol, acetone, carbon tetrachloride and citronella oil were mixed together in equal parts in order to observe the cleaning effect on birch bark.

As in the case of other chemicals, bark pieces were kept dipped in the mixtures for 2 hours. The samples were taken out of the mixture and excess solution was removed by pressing them under a blotting paper, applying 10 kg pressure. Drying was done at room temperature.

It was observed that with the above mixture the bark samples had become soft and flexible. On the natural bark, there is a whitish natural deposit. This deposit disappeared with the mixture and in its place a yellowish brown colour appeared. Although the constituent layers of birch bark did not separate out, natural adhesive property had been lost to some extent. There was no change in the physical strength of the bark as such.

Obviously, because the bark samples had become more flexible and soft, this mixture of chemicals cannot be used for cleaning of the bark.

b) The second set of mixture was composed of trichloroethylene, methanol and glycerine. They were mixed in equal quantities (v/v). Sample pieces of specified sizes (215 cm^2) were placed in the solution for about 2 hours and the effect of chemicals on them was studied.

There were considerable wrinkles over the surface of the bark. A dark brown with oily appearance appeared on the surface. It seemed that the cleaning mixture dissolved out organic contents of the bark, from the surface.

c) The third mixture was composed of ethylene (70 percent), trichloroethylene and glycerine mixed together in equal parts (v/v).

There was considerable softness in the bark, possibly due to the absorption of glycerine in the material. The original colour of the bark is also changed to slight brownish shade. However, the individual layers of the bark did not separate from each other.

The change in the colour of the bark before and after treatment with cleaning agents as measured with Gloss Reflectance Meter (AIM/611). Results are mentioned in Table-I.

PART-II

STUDIES OF THE EFFECT OF BLEACHING AGENTS ON BIRCH BARK

The following chemicals were used as bleaching agents to study their effect on birch bark.

1. Chloramine - T
2. Sodium Chlorite
3. Hydrogen peroxide
4. Hypochlorite

N-Chloro-p-toluene sulphanomide has been used as a bleaching agent for paper.

Birch bark samples of 2.5 cm^2 were used for ascertaining the bleaching effect of chemicals on the natural colour of the bark.

The samples were dipped in the solutions of 1, 1.5 and 2 percent concentrations for 24, 48 and 72 hours durations at room temperature in closed containers.

The effect of the chloramine-T solution was observed on the bark after 24 or 48 hours in any of the concentrations. However, after 72 hours of dipping, lenticles of the bark were found to be discoloured in all the concentrations. No other side-effect of the chemical was found on the bark. The physical strength remained the same. The layers of the bark did not separate out.

Table II presents the results of various observations.

Sodium Chlorite

Sodium chlorite is another bleaching agent used for bleaching paper. It was also prepared in three concentrations, i.e. 1, 1.5 and 2 percent. The samples of 2.5 cm^2 were kept immersed in the solution for about 3 hours.

No bleaching action on the natural colour of bark was observed even after 3 hours duration. At this point, solutions were acidified with HCl (N) solution to bring the pH to below 4.0. Chlorine dioxide started to be evolved and the bleaching reaction commenced. In alkaline or neutral solutions, sodium chlorite has no bleaching effect and the chemical is to be activated by acidification to a pH below 4.0.

More bleaching effect was observed with higher concentrations of sodium chlorite and hence the brightness increased gradually. The bleaching effect was seen more on the lenticles of bark which changed from dark brown to yellowish white. There was no separation of layers in 1 and 1.5 percent of solutions. However, 2 percent solution had the tendency of loosening the layers. There was no reduction in the physical strength of the bark at lower concentration of sodium chlorite.

Table II presents the results.

Hydrogen Peroxide

The bleaching effect of hydrogen peroxide on birch bark samples was observed as follows:

1. Sample of 2.5 cm^2 were treated with hydrogen peroxide solution for 24 hours at room temperature in closed containers. No effect was noticed.

2. The bark samples were treated with hydrogen peroxide along with alkaline solutions of 1, 1.5 and 2 percent concentrations. In this case, a bleaching effect on bark was observed. Reaction of hydrogen peroxide in alkaline medium produces nascent oxygen which helps to bleach the samples by oxidation. It may be mentioned that lignin is not affected appreciably by this process. But the organic colouring matter changes appearance. The samples were treated with alkaline hydrogen peroxide for 3 hours, the bleaching effect was more at higher concentrations of alkalinity. Discolouration is observed more on lenticles of the bark. The layers of the bark separated in all

the cases.

3. The bleaching effect of alkaline hydrogen peroxide solution (NaOH) on 1, 1.5 and 2 percent concentration was tested at 80 to 85°C temperature for 3 hours. At the end of the experiment, the bark changed from dark brown to blakish in colour. More effect was observed in lenticles. The layers also separated. The shiver effect on bark was observed at higher concentration of alkaline hydrogen peroxide. The physical strength of the bark samples as also considerably reduced.

Hypochlorite (Bleaching Powder)

Bleaching with hypochlorite solution was carried out by using bleaching powder. To prepare the solution, 10 gm of bleaching powder was made into a paste with a little quantity of water and then diluted with distilled water. The precipitate was allowed to settle for some time and the clear solution was decanted in a 1 litre graduated volumetric flask. This operation was repeated several times, until all the solid matter was transferred to the flask. The solution was made up to 1 litre and mixed well. It was kept over night and mixed to allow the precipitate to settle. The available chlorine was determined with iodometric titration method. It was found to be 0.0088 percent.

Birch bark samples of 2.5 cm² were dipped in three solutions of bleaching powder, containing available chlorine respectively as 0.0018 gm, 0.0026 gm and 0.0035 gm for 48 hours duration at room temperature. A very slow bleaching effect was observed. At the end of 48 hours the appearance changed considerably, almost in all cases.

Table II presents the results.

PART-III

STUDY OF THE EFFECT OF ADHESIVE ON BIRCH BARK

The following adhesives were tested for their utility in the conservation of birch bark manuscripts.

1. Methyl Cellulose
2. Soluble Starch
3. Carboxymethyl cellulose
4. Animal glue (Commercial)
5. Polyvinyl acetate

The bark samples of 2.5 cm² were prepared. Pastes of adhesives were prepared in 3 different consistencies i.e. 1, 1.5 and 2 percent. They were applied in between the layers of bark with soft hair brush and dried at room temperature.

The pasted samples were kept in an oven at 80°C for 24, 48 and 72 hours duration. The effect was observed in all the samples at the end of the experiment. The samples were also kept at 105°C temperature to find out further effect, if any.

Observations were made regarding separation of layers, the sticking property of adhesives, and the change in the brightness.

Results are given in Tables III and IV.

CONCLUSION

On the basis of the experimental results it may be concluded that:

The aqueous cleaning may not be harmful to birch bark manuscripts. Among the non aqueous methods, organic solvents like xylene, carbon tetrachloride and trichloroethylene are found suitable for cleaning. Some of the organic solvents alongwith the mixture of glycerine and citronella oil are also found suitable.

In the case of bleaching agents, all the chemicals have been found to have some bleaching effect on bark samples. However, observations were that H₂O₂ at room temperature may be useful to bleach stains from the manuscripts of bark.

In the case of adhesives, some of the adhesives like methyl cellulose and carboxymethyl cellulose gave good results and may be useful to refix the separated layers of bark. Even at their lower consistency the effect of above adhesives show good sticking property, before and after artificial aging.

The study of adhesives on birch bark is preliminary but results of different parameters given in Table III and IV show encouing results to undertake further studies on the behaviour of different adhesives in relation to birch bark.

REFERENCES

1. Agrawal, O.P., Gupta, C.B. and Suryavanshi, D.G., Conservation and Study of the Properties of Birch-bark, ICOM Committee for Conservation Meeting, Preprints, Copenhagen, 1984, 84.14.1.

TABLE I, EFFECT OF CLEANING AGENTS ON BIRCH BARK

Sl. No.	Cleaning Agents	EFFECT ON CLEANING AGENTS ON			
		Separation of Thin Layers of Birch bark	Appearance of bark	Brightness %	
				Before cleaning	After cleaning
1.	Tap water				
	Cold	N	N	44	37
	Hot	N	N	45	33
2.	Distilled water				
	Cold	N	N	46	41
	Hot	N	N	45	42
3.	Organic solvents				
	Acetone	Y	LC	45	36
	Alcohol	Y	LC	46	39
	Ether	Y	LC	45	37
4.	Carbon tetra-chloride	Y	N	46	39
5.	Trichloroethylene	N	N	47	41
6.	Xylene	N	N	45	39
7.	EtOH+CCl ₄ +Acetone +Citronella oil	Y	Bark becomes soft,flexible and oily	44	38
8.	Trichloroethylene+ MtOH+Glycerine	Y	Shrinkage of bark soft and flexible	44	27
9.	70% EtOH+Trichloro-ethylene+Glycerine	Y	Soft and flexible	44	23

N=Nil, Y=Yes and LC=Little change

TABLE II, EFFECT OF BLEACHING AGENTS ON BIRCH BARK

Sl. No.	Bleaching Agents	EFFECT OF BLEACHING AGENTS ON			
		Separation of Thin Layers of bark	Appearance of bark	Brightness %	
				Before Bleaching	After Bleaching
1.	Chloramine-T				
	%				
	1.0	N	N	63	55
	1.5	Y	C	63	57
	2.0	Y	C	63	52
2.	Sodium Chlorite				
	%				
	1.0	N	N	36	43
	1.5	N	N	36	53
	2.0	Y	C	36	63
3.	Hydrogen Peroxide				
	A. As such treatment for 24 hours	N	N	26	38
	B. Alongwith NaOH at room temperature				
	%				
	1.0	Y	N	53	26
	1.5	Y	C	53	30
	2.0	Y	C	53	40
	C. Alongwith NaOH at 80-85°C temperature				
	%				
	1.0	Y	C	57	26
	1.5	Y	C	57	18
	2.0	Y	C	57	13
4.	Bleaching Powder (Hypochlorite)				
	0.0018 gm Cl	Y	C	37	46
	0.0026 gm Cl	Y	C	37	55
	0.0035 gm Cl	Y	C	37	52

N=Nil, Y=Yes and C=Change

TABLE III, EFFECT OF ADHESIVES ON BIRCH BARK AT 80°C TEMPERATURE FOR 24, 48 AND 72 HOURS AGING

Sl. No.	ADHESIVES %	EFFECT OF ADHESIVES ON									
		Separation of bark layers after aging for hours			Sticking Property of bark after aging hours			Brightness of Bark %			
								Before aging	After aging for hours		
		24	48	72	24	48	72		24	48	72
1.	Methyl cellulose										
	1.0	N	N	N	G	G	G	31	26	24	26
	1.5	N	N	N	G	G	G	31	28	24	25
	2.0	N	N	N	G	G	G	31	29	26	25
2.	Soluble starch										
	1.0	Y	Y	Y	N	N	N	40	36	32	37
	1.5	Y	Y	Y	N	N	N	40	38	35	35
	2.0	Y	Y	Y	N	P	P	40	39	36	37
3.	Carboxy Methyl cellulose										
	1.0	Y	N	N	P	G	G	40	33	32	36
	1.5	N	N	N	G	G	G	40	28	34	40
	2.0	N	N	N	G	G	G	40	38	37	31
4.	Animal glue										
	1.0	Y	Y	Y	P	P	P	52	51	44	41
	1.5	Y	N	Y	P	P	P	52	55	43	45
	2.0	Y	N	Y	P	G	P	53	50	39	36
5.	Polyvinyl Acetate										
	1.0	Y	Y	Y	P	N	P	39	28	26	24
	1.5	Y	Y	Y	P	P	P	39	28	28	28
	2.0	Y	Y	Y	P	P	P	39	31	23	27

N=Nil, Y=Yes, G=Good and P=Poor

TABLE IV, EFFECT OF ADHESIVES ON BIRCH BARK AT 105°C TEMPERATURE FOR 24, 48 AND 72 HOURS AGING

Sl. No.	ADHESIVES %	EFFECT OF ADHESIVES ON									
		Separation of bark layers after aging for hours			Sticking Property of bark after aging for hours			Brightness of Bark %			
								Before aging	After aging for hours		
		24	48	72	24	48	72		24	48	72
1.	Methyl cellulose										
	1.0	N	N	N	G	G	G	25	22	21	23
	1.5	N	N	N	G	G	G	26	25	24	19
	2.0	N	N	N	G	G	G	27	27	21	15
2.	Soluble starch										
	1.0	Y	Y	Y	N	P	N	35	36	27	31
	1.5	Y	Y	Y	N	P	N	36	34	34	34
	2.0	Y	Y	Y	N	P	N	37	38	29	28
3.	Carboxy Methyl cellulose										
	1.0	Y	Y	N	P	P	G	34	30	30	32
	1.5	N	N	N	G	G	G	34	26	30	35
	2.0	N	N	N	G	G	G	35	33	29	28
4.	Animal glue										
	1.0	Y	Y	Y	P	P	P	48	49	49	55
	1.5	N	N	Y	P	P	P	44	55	46	51
	2.0	N	N	Y	P	G	P	42	51	45	30
5.	Polyvinyl Acetate										
	1.0	Y	Y	Y	N	N	P	26	28	24	21
	1.5	Y	Y	Y	P	P	P	28	29	28	27
	2.0	Y	Y	Y	P	P	P	27	33	18	25

N=Nil, Y=Yes, G=Good and P=Poor

SUMMARY

Completion of parchment manuscripts deteriorated as a result of biological effects is a very complicated task and although several different methods are applied for this purpose, none of them may be considered suitable for the restoration of severely damaged leaves.

In 1983 experiments on the completion of parchment leaves by manual casting started in the Hungarian National Library /Országos Széchényi Könyvtár/. The aim was to join the lacunae of the extremely weak manuscripts and simultaneously to consolidate the parchments as well as to fix the inks and pigments on the support. The most appropriate composition for the pulp was chosen on the basis of physical examinations, aesthetic considerations and stability. The study presents the details of the procedure.

REPORT ON PARCHMENT CODEX RESTORATION BY PARCHMENT AND CELLULOSE FIBRE PULP

Ildikó Beöthy-Kozocsa
National Széchényi Library
H-1827 Budapest, Hungary

Dr. Teréz Sipos-Richter
Research-Development Company for the Leather and Shoe Industry
Chemical Development Department
H-1047 Budapest, Paksi J. u. 43. Hungary

Györgyi Szlabey
Eötvös Loránd University /Budapest/
University Library
H-1053 Budapest, Károlyi Mihály u.10. Hungary

Introduction

When stored under unfavourable climatic conditions parchment codices may experience physical, chemical and, in due course, biological damage as a result of direct moistening. The harmful effects bring about the undulation/curliness and deformation of the leaves of the codices. Microorganisms proliferated to a dangerous extent result in the degradation of the collagen fibres of the parchment as well as that of the binding agent of the inks and pigments on it. The process is furthered by a decrease in pH value, a slight acidification of the parchment which takes place as a result of atmospheric agents /the high sulphur-dioxide content in the air/. The pigments produced by the microorganisms discolour the surface of the codex leaves, the parchment in the affected areas grows thinner and becomes fluffy and feeble; at the very worst the skin tissue is completely destroyed. The inks and pigments on the support become cracked, detached and faded.

Such accumulated deterioration appeared on the 15th c. codices of the Budapest University Library which were returned to Hungary in 1877 after having been kept in Turkey for about 350 years. From among the 34 codices 12 are authentic Corvinas from King Matthias' library. The codices which have experienced many vicissitudes may often have been exposed to environmental conditions when - as a result of damp atmosphere or direct moistening - the so far inactive spores could turn active and develop their colonies. Today, however there are a number of microbic colonies to be observed by the naked eyes - owing to whose deteriorating activity the parchment was partially lost - from which it is practically impossible to cultivate any microbes. Probably lacking subsequent sources of humidity these colonies dried out and their cells have been partially or fully destroyed. The same can be stated concerning the remains of the mites to be found on several leaves of the codices.

Nevertheless, microbiological examinations confirmed that from among the characteristic red, purple and violet discolourations the microbes which have brought about the red discolouration and other grave deformations belong to the branch of the *Streptomyces fomicarius*. /1/ It is a strange phenomenon that along the letters and in their immediate vicinity there is no red discolouration to be found which indicates that the *Streptomyces fomicarius* avoids ink containing gum-arabic and lamp-black. On several codices colonies of *Penicillium* sp. and *Alternaria* sp. were also identified. /2/ In Photo 1 the top right corner of the 15th c. *Albucasis* codex is presented. By sampling with a self adhesion tape the branching of the penicilli of *Penicillium* sp. and the broken off conidia of the reproductive organs could be found /Photo 2/. In Photo 3 the penicilli of a *Penicillium* sp. are shown from a culture. Specimen was taken with a throat swab and inoculated onto a fungus cultivation agar medium.

Standard procedures cannot be applied successfully for the conservation of codices severely damaged by microorganisms. Such techniques include among others the completion of fragmented parts by new paper or parchment, the covering of the weakened areas by natural or synthetic fabrics /lamination/ or the impregnation of the leaves by various reinforcing solutions.

We were looking for a method by which the material used for the replacement of the lost parchment could be bound permanently to the already thin and feeble original with an appropriate transition in between. The strains between the completing and the original material have to be reduced to a minimum, since the stresses originating from differences in the thickness, solidity

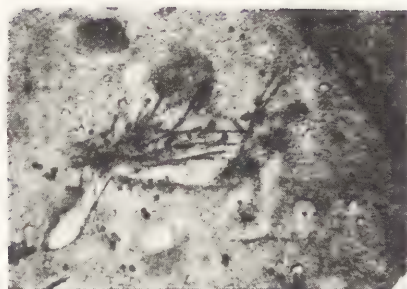


Fig.2: Fungal hyphae and conidia of *Penicillium* sp. on the Albucasis codex

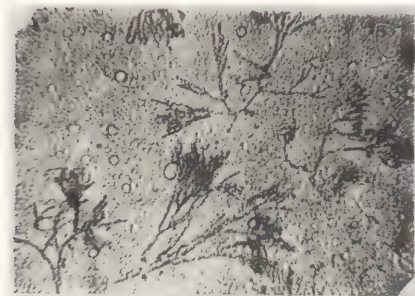


Fig.3: The penicilli of *Penicillium* sp. cultivated from the Albucasis codex

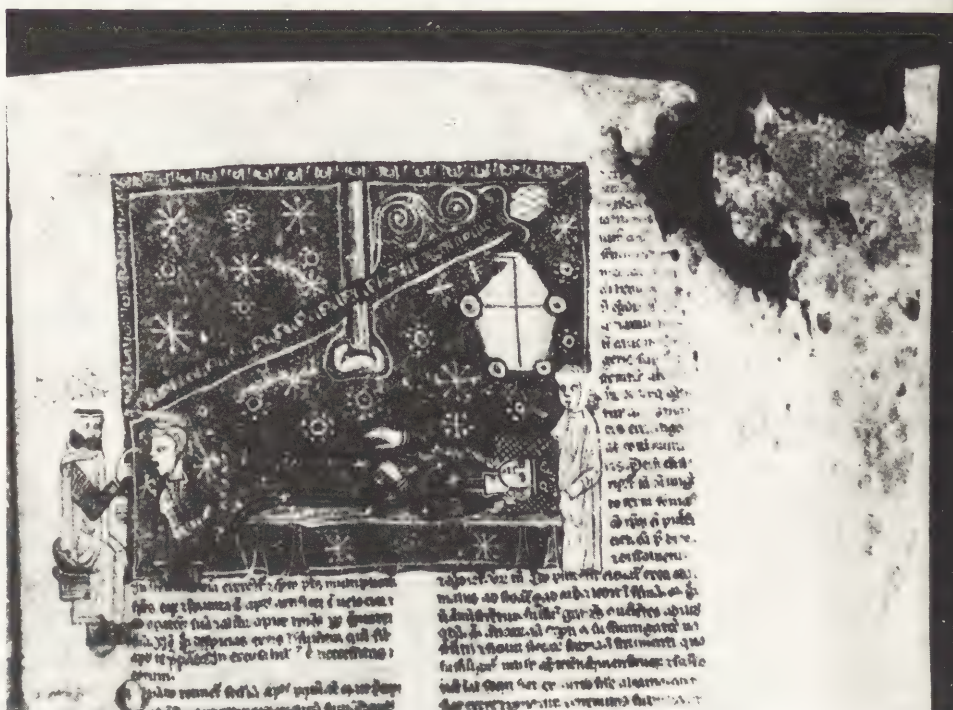


Fig.1: Leaf of the Albucasis codex from the 14th c.

and other physical properties of the two materials may bring about crimping of the restored leaf as well as result in further physical deterioration and tearing. We also wanted to achieve that the parchment support which has already lost its fastness should be conserved and fixed together with the damaged or loosened inks and pigments on it. At the same time we wanted to accomplish the preventive disinfection of the codices, too.

The widely known sheet forming procedure utilized in the restoration of incomplete documents made of paper seemed to be the most effective method. /In the course of paper casting the missing parts are replaced by paper pulp./ Obviously, the mechanical variety of paper casting cannot be applied with illuminated codices because neither the weak parchment nor the damaged inks and pigments could sustain the process in a medium abounding in water. Therefore, a procedure resembling manual paper casting but carried out on a vacuum table was seemed to be the best. In the past few years restorers have been experimenting with parchment sheet formation and several publications containing the results appeared. /3/ The substance applied in restoration was made of cellulose fibre, parchment powder or a combination of these two materials. As far as we know documents conserved in this manner have not been subjected to physical examinations yet.

For our experiments a mixture of parchment and cellulose fibres was applied.

The preparation of parchment codex leaves for the casting process

After the accomplishment of microbiological and chemical analyses, the contaminated codices were disinfected by a gas mixture of 15 % ethylene oxide and 85 % carbon dioxide /gas concentration: 500 g/m³, temperature: 25-30°C, relative humidity: 60 %, pressure: 0.7-0.3 kp/cm², operation time: 24 hours/. Then followed the mechanical cleaning of the codices after which the heavily crimped and deformed leaves were placed in a 1-2 % solution of p-chloro-m-cresol dissolved in isopropyl alcohol or methanol. P-chloro-m-cresol protects parchment against subsequent infection. Less crimped or flat leaves were not placed in the bath but were sprayed with the above solution right before casting. Extremely fragile and brittle parchments were placed into a bath with 2-8 % hydroxy-propyl-cellulose in it /the percentage depending on the condition of the leaf in question/.

Taking into consideration their sensitivity to solvents, damaged and cracking pigments as well as the separating inks were fixed permanently by microcrystalline/amorphous wax dissolved in carbon tetrachloride by water-colour brush. Gilding that was found, to be cracking or flaking off was brushed over by an emulsion containing egg-white /olvalbumin/. If, for whatever reason, we

wanted to completely avoid the moistening of the leaves, but had to fasten the pigments and inks, this was done by brushing them with a 5-10 % solution of hydroxypropyl-cellulose in isopropyl alcohol. As a preventive disinfectant p-chloro-m-cresol was added to it. The ink of one of our codices, which was non-illuminated but extremely crumbling, was affected by all organic solvents except ethylacetate. Before casting it was inevitable to consolidate the support and to fix the ink as well. This was done by a 2 % solution of a synthetic resin /30 % metacrylate, 70 % ethyl-metacrylate copolymer /in ethyl-acetate applying a retouch gun for pulverization.

After the baths and the fixing of pigments and inks the completion of the missing parts followed. In case the casting completing procedure did not commence at once after preparation, the wet parchment was dried and pressed even.

Completion by parchment and cellulose fibre pulp

The completion of gaps takes place by direct casting on the wet parchments, or in the case of lesser lacunae - when the aim is to protect the leaf from getting damp - the so-called dry method is applied. Casting on the vacuum table is employed only if the parchment and the inks as well as the pigments permit it, or once they have been protected.

The composition of the casting pulp

4 g parchment powder
4 g cellulose fibre
400 ml distilled water
3 ml 7 % solution of hydroxy-ethyl-methyl-cellulose
20 ml parchment glue
150 ml ethyl alcohol
50 ml isopropyl alcohol

Parchment powder: Picker, i.e. limed leather used for the propellers of the textile machines is cleaned, cut up by guillotine and pulverized on a grinding wheel fitted with a non-thermoplastic vehicle and is sifted.

Cellulose pulp: A mixture of cellulose fibre and various Japanese tissues is used to prepare a suspension as follows: 30g of fibre mixture is soaked in 2000 ml distilled water for 4 hours /dry substance: 1.5%/. The fibres of the Japanese tissues are separated in a laboratory disintegrator for 3 minutes; sulfide or sulfated pine cellulose is ground in Valley-beater and is dehydrated on a sieve until dry substance content reaches 15%. The suspension is preserved in 1-2% p-chloro-m-cresol calculated for the dry fibre content and dissolved in ethyl-alcohol.

Taking into account aesthetic considerations and the results of strength tests the following fibre composition seems to be one that works well:

- Hosokawa N° 634 500 paper	1 part
- Hodomura N° 644 461 paper	2 parts
- Rice paper N° 634 490 ₂ paper	2 parts
- Japanese tissue 9 g/m ² N° 25504 *	paper 1 part

Parchment glue: prepared as is usual in restoration practice./4/
The preparation of the casting pulp

Before preparing the casting pulp the parchment powder is swelled in 200 ml of water for 24 hours. The cellulose fibre suspension calculated for 4 g of dry substance and prepared as described above is also soaked in 200 ml of water and is mixed in a domestic or industrial blender for a few minutes after having added all the ingredients in the following order: cellulose fibre suspension, hydroxy-ethyl-methyl-cellulose suspension, parchment glue and alcohols. It is not advisable to use the freshly made and foamy pulp. It should be allowed to stand for a couple of days and stirred at intervals. If need be, the pulp may be dyed to match the colour of the parchment to be completed. In Photo 4 a restored leaf of Cod. Lat. 26 is shown. On the annexed diagram the drawing illustrates the cast areas.

Casting on wet parchment leaf

The casting of parchment is carried out on a table that can be lit from below and is fitted with a vacuum air-pump. About 8-12 filter papers, boards and weights as well as the casting pulp and a small

* Paper N° 25504 is from the Vangerow catalogue, the others are from the Drissler catalogue.



Fig. 4a.: Sketch: those places where casting was made

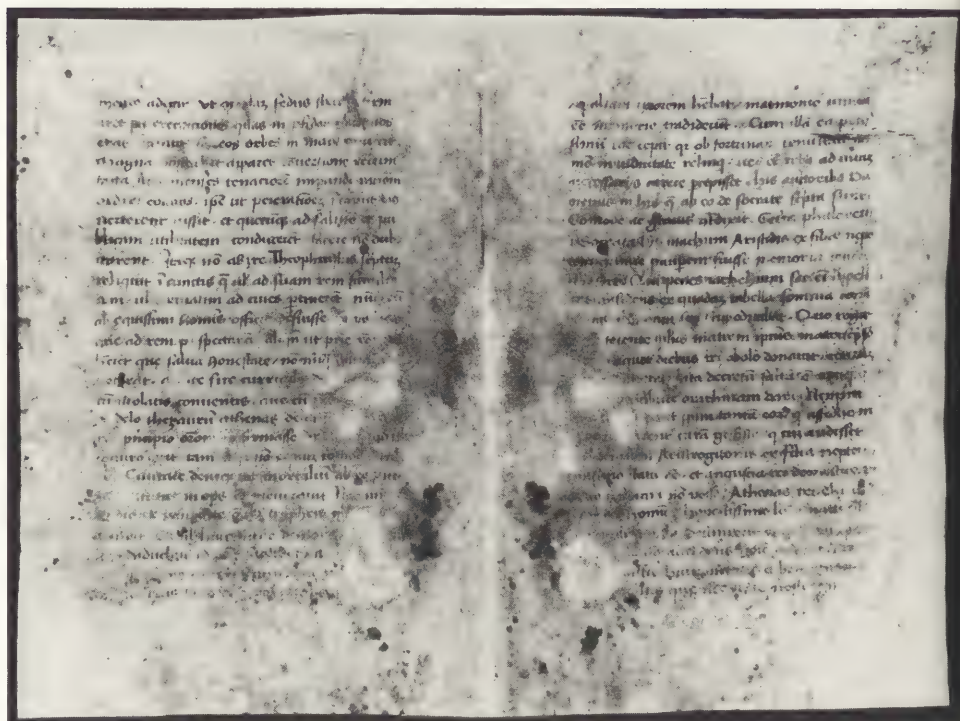


Fig. 4.: Codex leaf restored by casting

synthetic container/flacon in which the pulp is to be filled are prepared. The flacon should be light and handy so that casting can be carried out with ease. Polyamide screening cloth is placed on the perforated plexiglass board of the vacuum table which is covered by a Diolen silk weave fabric sprayed with 70% ethyl alcohol. The parchment codex leaf which has been pretreated as described above and conditioned in between wet filter papers is laid on the Diolen fabric. In case the parchment is already dry, a mixture of water and alcohol is sprayed on it. The vacuum motor is turned on as a result of which the parchment is pressed to the Diolen and casting may begin. In the areas to be completed the edges of the parchment leaf are slightly lifted and a small amount of pulp is poured onto the Diolen at the edges of the gap. In this manner we can avoid the need to cast the reverse side of the parchment once it becomes dry. When joining extensive gaps casting should be done continuously, proceeding in the same direction, then at right angles and diagonally, finally in the places thinly cast concentrically. Casting should be broken off for short intervals so that the fibres may settle evenly in layers, otherwise the pulp has no time to be drawn in and it may slip and result in an uneven cast. Once we find that the cast is smooth and its thickness resembles that of the parchment, another piece of Diolen fabric - with filter paper on each side - is placed on the cast parchment leaf which is then slightly pressed between boards. It is left to dry for a short while, then the filter paper is replaced and pressing follows with heavier weights this time. A few minutes later the Diolen fabric is carefully lifted from the cast spots, the filter papers are replaced and once again it is allowed to stand. Shortly afterwards if the casting along the lacunae covers bits of the text the surplus may be carefully removed with a scalpel and the wet casting may be thus corrected. Once the parchment leaf has become dry it is placed in between two polyester sheets and filter paper and is pressed starting by small pressure which is increased later on. It is important to replace the wet filter papers by dry ones occasionally. The cast leaves are usually left in the press for 2-3 weeks. The quality of the restored parchment depends to a great extent on the care taken while drying. The drier the leaves, the greater pressure may be applied. It is essential to judge the duration of drying and the amount of pressure to be exerted correctly.

The application of casting pulp on dry parchment leaf

The vacuum table is not the only means for the application of casting pulp on parchment. In case we wish to avoid the wetting of the parchment the following procedure may be employed: blotting paper, felt and Diolen are placed on the bench and a disc-shaped cast is poured on the fabric. The moisture is taken up by the felt and the blotting paper and a continuous sheet is formed. Using a scalpel pieces whose size corresponds to the lacunae in the

parchment may be taken up from the slightly desiccated cast. In this way small holes brought about by gnawing, tears and losses may be completed. The dry parchment leaf under which Diolen fabric and blotting paper are placed draws in the moisture and the binding agents ensure the sticking of the cast. A scalpel or other levelling tools /bone/ may be employed to obtain the thickness of the parchment from the still moist and plastic cast. After having joined all the lacunae, Diolen fabric, blotting paper and boards are placed on the parchment leaf which is then dried as described above.

Surface treatments

The treatment of the whole surface of parchment leaves is required only in exceptional cases. Such instances are: a/ when the parchment leaf continues to be very weak after pre-treatment and casting; b/ there are a number of holes and cracks which cannot be restored without partially covering the text.

In the first case before the complete desiccation of the restored leaves a layer of hydroxy-propyl-cellulose dissolved in ethyl-alcohol is applied by spraying or brushing. Its concentration is chosen to confirm the condition of the parchment. If the codex is not illuminated and the ink is sufficiently water-proof, 1:1 mixture of parchment glue and ethyl alcohol may be applied for the treating of the surface.

As for the second case, there may be a need for the partial or full embedding /mounting/ of the leaves. It goes without saying that miniatures are not to be covered. Mounting should be done by a perfectly transparent material as we cannot end up making the usually faded text even less legible. For our purposes fine polyamide fabric or gold beaters skin was found to be best. The sticking of polyamide was carried out by the following adhesive mixture: 2 parts of thick rice or wheat starch, 1 part of hydroxy-ethyl cellulose and 1 part of polyvinyl acetate. For the mounting of the gold beaters skin a mixture of wheat starch and parchment glue taken in an equal proportion was used. To the adhesives a 2% solution of p-chloro-m-cresol dissolved in isopropyl alcohol was added.

Examination of restored parchments

To test the tearing strength and resistance to permanent folding of new and old parchment samples, leaves made of the casting pulp and 15th-16th cc. parchment fragments completed by the new method were examined.

Before testing the samples were conditioned at room temperature and 65% relative humidity for 48 hours. Tearing tests were carried out by an Instron 1112 type tensile strength machine. Permanent folding was measured by the Bally flexometer, usually applied for the testing of leather. The test results are presented in the tables below.

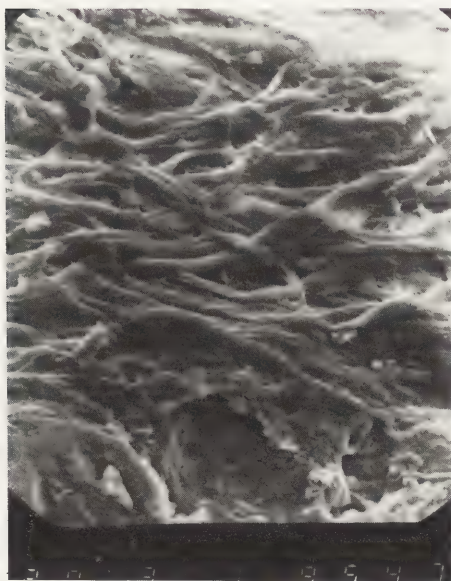


Fig.5.: Photo taken by an electron microscope of the unwritten surface of a 16th c. parchment fragment, 300x

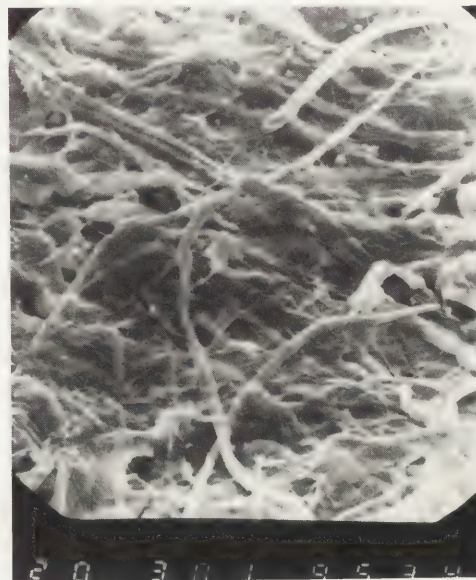


Fig.6.: The surface of a cast sheet under electron microscope, 300x

Sample	Direction	Average thickness mm	Breaking strength ₂ N/mm
1. new Italian parchment for writing	longitudinal	0.317	43.60 \pm 1.86
	transverse	0.280	53.38 \pm 2.49
2. new Italian parchment for writing	average	0.292	36.32 \pm 2.11
16th c. parchment	average	0.249	35.39 \pm 17.32
15th c. parchment	average	0.257	82.80 \pm 13.6

The Italian parchments for writing No. 1 and No.2 originate from two different pieces. The strength values for old parchments are strikingly high, however, the standard variation is considerably greater than that of the new material.

When testing samples taken from the casting pulp, only the composition of the cellulose fibre was modified. Cellulose fibres were obtained from various Japanese tissues as well as from fibres used in the paper industry. After soaking the Japanese papers were separated in a disintegrator; they were not ground and therefore the length of the fibres and the grade of grinding was determined by the procedures during the preparations involved in paper making. The fibre composition of the papers was determined by the Research Institute of the Paper Industry Company and is presented in table below.

Composition of fibres %	Hosokawa	Hodomura	Japanese tissue	Ribe paper Rice
Gampi	80-75	10-15	90-95	- -
Pine cellulose	20-25	70	5-10	20-25
Chemical fibres from deciduous wood	-	10-15	-	- -
Rice straw	-	-	-	75-80

Casting pulp was prepared from the cellulose fibre pulp suspension and the additives. The next table contains the values for the cast sheets and the fragments completed by casting.

The sample made of Hodomura fibres was the only one which did not tear along the boundaries. Therefore we made an attempt to use a mixture of the fibres. The next table presents the values of tensile strength and folding resistance for sheets made of mixed fibres and the fragments completed by casting.

Taking the results of folding resistance into account we chose Fibre Composition No. 4 for further experiments.

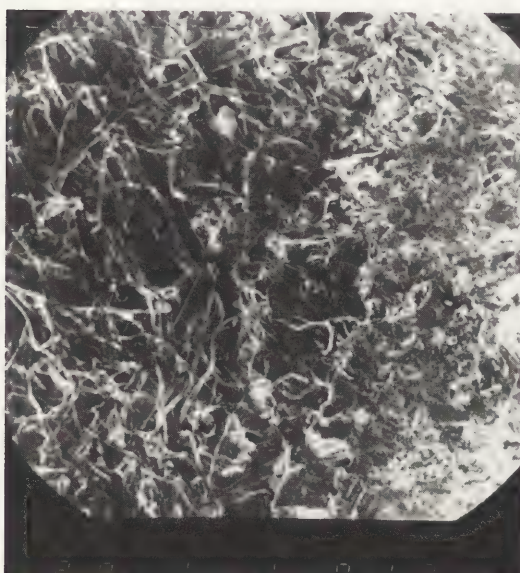


Fig.7.: Overlapped area of the original and the newly cast parchment, 100x

Composition of cellulose fibre	Average thickness mm	Tearing strength N/mm ²		Notes
		Cast sheet	Fragments completed by casting	
Japanese tissue /9g/m ² / SR ^o 14	0.185	3.4	3.7	+
Rice paper SR ^o 26	0.217	2.0	2.3	+
Hodomura SR ^o 14	0.168	12.0	6.3	
Hosokawa SR ^o 18	0.203	2.05	2.1	+
Bleached sulphated pine pulp SR ^o 18	0.171	18.8	4.5	+
Bleached sulphide pine pulp SR ^o 16	0.188	12.0	5.8	+

+ The fragments completed by casting tore along the boundaries of the old parchment and the new sheet.

Composition of cellulose fibre	Tensile strength N/mm ²		Notes	Bally resistance to folding, cycle
	Cast sheet	Fragments completed by casting		
Japanese tissue /9g/m ² / 1: rice paper 1	9.9	6.7	+	2
Hodomura 1: rice paper 1	27.5	18.3		800
Hodomura 4: rice paper 1 Japanese tissue /9g/m ² / 1	29.2	18.7		10
Hodomura 2: Hosokawa 1: rice paper 2: Jap.tissue /9g/m ² / 1	31.8	20.4		>1500
Hodomura 2: rice paper 2 cotton cellulose 2: bleached sulphide pine pulp 1: Jap.tissue /9g/m ² / 1	24.9	17.1		10
Hodomura 2: rice paper 2: Jap.tissue /9g/m ² / 2: cotton cellulose 2	32.7	18.1		10

+ Samples of fragments completed by casting tore along the boundaries of the old and the new material.

We also examined the interrelation between the length of the cellulose fibre and the strength characteristics of the cast samples. We had the percentage composition of the length of the various fibres in the suspension determined following which the suspension was beaten with the beating degree set at various values between 14 and 80 SR^o. The data are not presented here since so far we could not establish with any certainty that there should be an interrelation between the length of the fibres and the values for strength.

The experience gained, however, shows that it is advisable to use fibres of medium beating degree /below SR^o 30/ and that in the region of SR^o 80 cast samples become transparent.

References

1. Zsuzsa Szabó - István Mihály Szabó: Mikroorganizmusok részvételének igazolása a Korvinák pergamen anyagának biodeteriorációjában. /Verification of contribution of microorganisms to the biodeterioration of writing parchment in Corvina codices. =Műtárgyvédelem, Budapest, 1984. 13. 87-95. p.
2. For Dr. Ervin Novák
3. Johannes Sievers: Fehlstellenergänzung bei Pergament durch Anfasern. = Maltechnik-Restaur, München, 1979. 3. 209-210.p.
Bruno Ruchatz: Anginessmethode mittels Pergament-Papierbrei.= Sonderdruck beim IADA Anfaserkurs am 10.6. 1982 in Schlitz.

Per M. Laursen: "Trockene" Pergament-und Papieranfaserung.
= Maltechnik-Restauro, München, 1985. 4. 63-66. p.
Ildikó Beöthy-Kozocsa: Új kísérletek a pergamen kéziratok restaurálására. /Recent experiments for conservation of parchment codices/. = Műtárgyvédelem, Budapest, 1984. 13. 75-84.p.

4. Otto Wächter: Restaurierung und Erhaltung von Büchern, Archivalien und Graphiken. Wien-Köln-Graz, 1982. 164.p.

SUMMARY

The level of paper stability was studied during processing of the 3 kinds of paper with 4 stabilizing solutions. It is found out that the index of folding endurance retention equal to 0.5 for paper made of cotton cellulose and subjected to artificial heat aging at 102-2 °C during 12 days can serve as a measure of paper stability after stabilization and restoration processes. In addition it is ascertained that paper sample made of cotton cellulose at 300°C in the process of pyrolysis when thermoanalyzing.

ESTIMATION OF PAPER STABILITY

M.G. Blank, S.A. Dobrusina
M.E. Saltykov-Shchedrin State Public Library
18, Sadovaya
191069 Leningrad, USSR

The development of methods and materials for stabilization and restoration of documents involves investigations of the model samples of paper subjected to some treatment. Changes in the paper structure, resulting from the accelerated artificial aging are identified by studying mechanical, chemical and optical properties of paper. To estimate the effectiveness of the treatment used one should compare the changes of the paper properties in the process of aging for control samples and those subjected to the treatment. It seems, however, expedient to introduce a certain level of paper stability as a reference mark for such investigations. The level should correspond to a certain service life of a document in the process of its storage and handling. An attempt to find some approach to the problem is a point of the present paper. The effect of the stabilizing solutions preventing the action of the physical-chemical damaging factor studied, the level of the paper stability was set. Model samples of the paper comprising 100% of cotton cellulose, 100% sulphite cellulose and newsprint were treated by solutions of 4 types: for composition see Table 1. Both treated and untreated (control) samples were subjected to accelerated aging in tightly closed glass pipes for 12 days at temperature 102-2 °C the initial amount of moisture being kept. This period of aging is supposed to correspond to 100-120 years of natural aging [1]. To estimate the changes of the properties of all kinds of paper the following values were measured: folding endurance, water extract pH, brightness. These tests are considered to be reliable characteristic of the process occurring in paper while aging and are easy enough in operation. Fig. 1 offers the changing of the values studied.

Table 1
Characteristics of the solutions for paper stabilizing

Type of solution	Chemical composition	Solvent	Method of introduction	Alkali reserve, %	Reference
Barrow's buffer (Bar.)	$\text{Ca}(\text{HCO}_3)_2$ $\text{Mg}(\text{HCO}_3)_2$	Water	Immersion	3	[2]
Chelate compound DTPA + Bar.	$\text{C}_{14}\text{H}_{23}\text{O}_{10}\text{N}_3$ + $\text{Ca}(\text{HCO}_3)_2$ $\text{Mg}(\text{HCO}_3)_2$	Water	Immersion	3	[2]
Methoxy magnesium methyl carbonate (MMMC)	$\text{CH}_3\text{OMgOCO}_2\text{CH}_3$ $\times \text{CO}_2$	Trichloro-trifluoroethane, Methanol	Immersion	1	[4]
Magnesium ethyl carbonate (MEC)	$\text{C}_2\text{H}_5\text{OMgOCO}_2$ $\times \text{CO}_2$	Trichloro-trifluoroethane, Ethanol	Spraying	1	[4]

Then the retentions of the three property indexes under study were calculated after 12 days of aging as a ratio of final and initial values for all kinds of paper. Table 2 shows the results of these calculations. The study of the Table 2 data proves the retention of the folding endurance to undergo most considerable changes and, therefore, it may serve as a measure of paper stability better than the other two indexes. The retention of the unstabilized cotton cellulose paper sample is 0.55. The cotton cellulose paper being able to serve as a pattern of stability and the above value of the retention being considered, we choose the stability level 0.5 as a measure for all kinds of paper. The treatment of the cotton cellulose paper with stabilizing solutions is proved by the experimental data to increase the above value.

The sulphite cellulose paper reduces its endurance considerably due to aging, so that its retention makes only 0.08. The stabilization treatment permits the retention to increase beyond the chosen level (0.5) in all the cases considered.

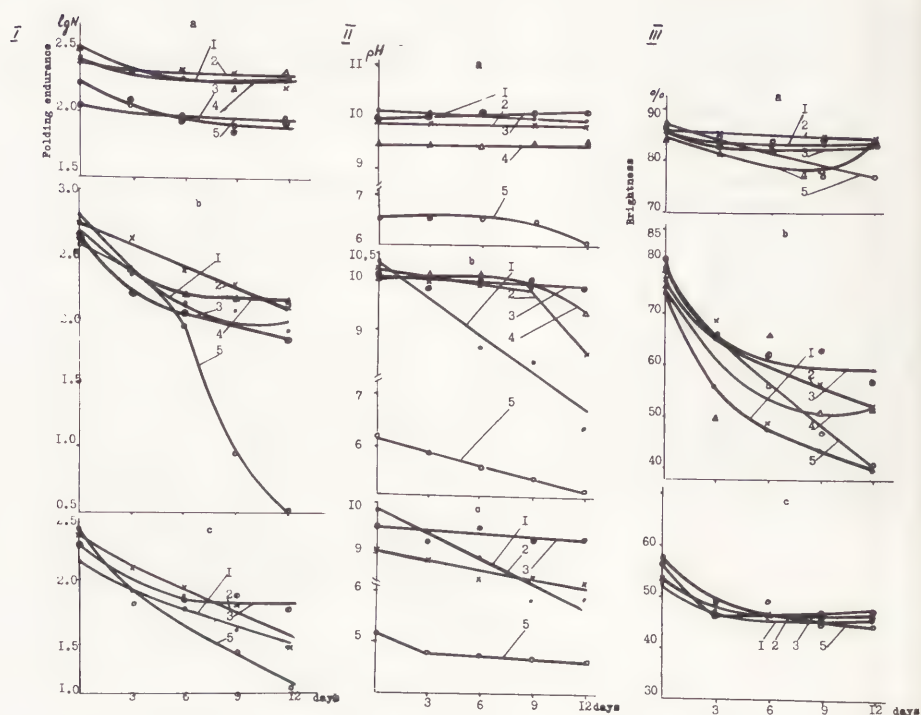


Fig. 1: Changing of properties of the paper subjected to stabilization and artificial aging.

a - cotton cellulose, b - sulphite cellulose, c - newsprint; I - folding endurance (N - number of double folds under load 9.8 N for "a", 6.9 N for "b", 5.9 N for "c"); II - water extract pH; III - brightness.

1 - Bar., 2 - DTPA + Bar., 3 - MMMC, 4 - MEC, 5 - control.

Newsprint retains only 0.04 of initial endurance in the process of aging. Stabilization leads to a increase of its folding endurance retention yet far beneath the accepted level (the highest value is 0.3). One may conclude that newsprint, besides the stabilizing solutions' treatment needs strengthening with any lamination method.

The changes of the pH values appears to vary far less than those of the folding endurance. Stabilization fails to affect the retention of this index in all cases, although it is sure to increase. At the same time the values of the pH retention obtained are quite close for all kinds of paper and any stabilization treatment in contrast to the folding endurance retention values.

Table 2
Relative indexes of paper properties after stabilization and artificial aging

Stabilization treatment type	Properties retention after 12-days aging with respect to the initial aging		
	Folding endurance	pH	Brightness
Cotton cellulose paper			
Control	0.55	0.92	0.89
Bar.	0.69	0.99	0.98
DTPA+Bar.	0.61	0.99	0.99
MMMC	0.84	1.0	0.96
MEC	0.75	1.0	0.95
Sulphite cellulose paper			
Control	0.08	0.84	0.54
Bar.	0.67	0.84	0.52
DTPA+Bar.	0.78	0.85	0.68
MMMC	0.70	0.98	0.71
MEC	0.79	0.98	0.70
Newsprint			
Control	0.04	0.88	0.77
Bar.	0.20	0.83	0.88
DTPA+Bar.	0.11	0.93	0.83
MMMC	0.30	0.97	0.69

Thus, measuring of the pH value in the artificial aging process is inexpedient due to low informativeness. To estimate the pH value of the water extract of paper after stabilization and compare it with pH 6 seems to be much more important, the latter value is supposed to be the lower limit still assuring the paper stability /2/.

Brightness retention is rather high for cotton cellulose paper, reduces by half for sulphite cellulose paper and less for newsprint. The stabilizing treatment leads to an increase of the retention in nearly all cases. The retention of newsprint, both treated and untreated (Fig 1 - III), has however turned out to be higher than that of sulphite cellulose paper. Brightness retention therefore fails to be considered a reliable characteristic of paper stability.

So the investigation conducted has proved the measurement of folding endurance value of the processed paper before and after 12 days of artificial aging (heating at 102-2 °C in hermetic pipes) to be sufficient for the conclusion of expedience of any treatment suggested. The obtained ration of the final and initial values should be compared with the accepted stability index value 0.5. If the value obtained is equal or exceeds the above value, one may consider the paper to be good for storage and handling for 100-120 years and finally to keep 50 or more percent of its initial strength. The water extract pH value should also be measured and be within the limits of 6-8.5. Exceeding the higher limit up to 10 is acceptable unless the text is undamaged. The above norms are introduced into the standard project "Conservation of documents. General demands".

Both stabilized samples of 3-4 types and control samples were subjected to thermogravimetric analysis. The pyrolysis of the paper samples was conducted in the air at MOM derivatograph OD-102 (Hungary), the constant speed of heating 3 °C/min being kept. The sample's mass was 50 mg. Fig. 2 shows the curves of the mass loss due to pyrolysis for the paper types investigated.

Thermograms are known to give a wide information concerning cellulose and paper /5/. The present work included calculation of the activation energy of cellulose thermodestruction for the maximum decomposition speed part according to the Horowitz-Metzger method /6/. The results are brought into Table 3. Every paper type has its own activation energy different from others. The highest value corresponds to cotton cellulose, the lower one - to sulphite cellulose and the lowest - to newsprint. Stabilization causes the increase of this value for all paper types. The sulphite cellulose paper increases its activation energy as far as near the cotton cellulose control sample one or even exceeds it.

Table 3
Changing of the mass of stabilized and unstabilized paper
due to pyrolysis and kinetic parameters

Stabilization treatment type	Activation energy, KJ/mol	Mass retention of paper with respect to the initial values while heating				
		100 °C	150 °C	200 °C	250 °C	300 °C
Cotton cellulose paper						
Control	226.4	0.96	0.95	0.95	0.95	0.94
DTPA+Bar.	264.6	0.97	0.96	0.96	0.96	0.95
MMMC	272.4	0.97	0.97	0.96	0.96	0.96
MEC	277.5	0.99	0.98	0.98	0.98	0.97
Sulphite cellulose paper						
Control	166.0	0.88	0.85	0.84	0.81	0.76
Bar.	186.3	0.95	0.94	0.93	0.92	0.90
DTPA+Bar.	193.2	0.91	0.88	0.86	0.85	0.80
MMMC	206.5	0.95	0.95	0.95	0.94	0.94
Newsprint						
Control	121.4	0.90	0.88	0.87	0.84	0.76
Bar.	125.4	0.92	0.90	0.89	0.86	0.80
DTPA+Bar.	129.1	0.95	0.93	0.93	0.92	0.87
MMMC	156.6	0.96	0.95	0.94	0.94	0.89

Fig. 2: Thermogravimetric curves for 3 types of paper (a - cotton cellulose, b - sulphite cellulose, c - newsprint), subjected to stabilization. 1 - Bar., 2 - DTPA+Bar., 3 - MMC, 4 - MEC, 5 - control.

At the same time the changing of the paper sample mass was studied at fixed temperatures from 100 to 300 °C. These limits correspond to the beginning of the cellulose pyrolysis following the loss of capillary water. The higher limit having been exceeded, cellulose depolymerization begins with abrupt increase of the

pyrolysis speed. Table 3 shows the values of the paper sample mass retention at 5 temperatures for the control and stabilized samples.

The increase of the mass retention of the stabilized paper samples over that of the control ones is observed at all temperatures studied. Moreover, this difference tends to increase noticeably at 300 °C especially to sulphite cellulose paper and newsprint. Comparing these results with those obtained above proves such a method of estimation of paper stability based on the mass loss at 300 °C to be informative. Mass retention of the cotton paper control sample (0.94) may be accepted as a measure of stability like the folding endurance retention. Again, as in the previous case, this measure of stability may be obtained, for example, for sulphite cellulose paper by MMMC or MEC solutions treatment. The obtaining of the necessary information by a single measuring at a small mass part of the sample without any extra calculations makes the advantage of the pyrolytic method of paper stability estimation.

Thus, two criteria of paper stability - stability indexes - are suggested as a result of the investigation conducted. The first, on the basis of the folding endurance value determined during the artificial heat aging, and the second, with the thermogravimetric curves used.

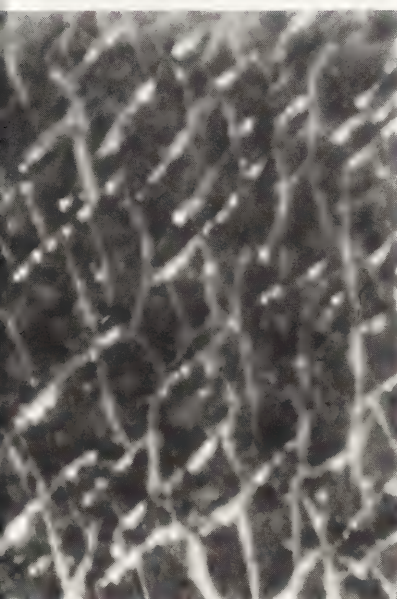
References

1. Roberson D.D. The evaluation of paper permanence and durability// TAPPI. 1976. Vol. 59, N 12. P. 63-69.
2. Permanence/durability of the book: Spray deacidification / W.J. Barrow research laboratory. Richmond (Va), 1964. N 3.62 p.
3. Blank M.G., Dobrusina S.A., Temkina V.J. Stabilizatsija bumagi kompleksnymi sojedinenijami. Soobshch. I // Teorija i praktika sokhraneniya knig v biblioteke/ M.E. Saltykov-Shchedrin State Public Library. L., 1983. Vyp. II. S. 47-61.
4. Wei T'o nonaqueous deacidification solutions and sprays / Wei T'o associates, inc. techn. information. Matteson (Ill.), 1982. 312-747-6660.
5. Blank M.G., Sazanov J. N. Ispolzovaniye metodov termoanaliza dla opredeleniya ctabilnosti bumagi razlichnoi kompozitsii // M.E. Saltykov-Shchedrin State Public Library. L., 1974. Vyp.6. S. 34-56.
6. Horowitz H.H., Metzger G. A new analysis of thermogravimetric traces// Anal. Chem. 1963. Vol. 35, N 10. P. 1464-1468.

RESUME

La détermination de la nature exacte des photographies est parfois difficile ou même impossible à effectuer par un simple examen visuel. Nous avons donc cherché à appliquer des tests complémentaires afin d'étudier les épreuves d'E. ATGET conservées dans les collections de la Ville de Paris. Des coupes transversales ont permis une étude stratigraphique différenciant bien la nature des 3 procédés de tirage (2 sans émulsion, 1 avec émulsion). L'analyse microchimique a permis d'identifier la présence d'albumine, d'amidon ou de gélatine dans les couches. Cette analyse par coloration a parfois été gênée par la tonalité brune des échantillons (prélèvements dans les marges) ou par la présence d'encaustique en surface. Nous avons ensuite analysé les éléments métalliques en présence par spectrométrie de microfluorescence X. Celle-ci en confirmant la nature des virages et des sels sensibles a permis de vérifier que les tirages analysés bien que de coloration parfois très diverse sont tous virés à l'or. Enfin, des essais microchimiques d'analyse des fibres ont été menés sur divers types de papiers photographiques anciens, avant d'être appliqués à une trentaine d'épreuves d'ATGET datant de 1890 à 1923. Cette période est particulièrement importante quant à l'évolution des supports.

IDENTIFICATION VISUELLE SOUS LOUPE BINOCULAIRE



Epreuve albuminée

TECHNIQUES D'ANALYSE APPLIQUEES AUX PHOTOGRAPHIES D'EUGENE ATGET CONSERVEES DANS LES COLLECTIONS DE LA VILLE DE PARIS

Anne CARTIER-BRESSON

Atelier de Restauration des

Photographies de la Ville de Paris

14, rue Payenne - 75003 PARIS - FRANCE

A l'occasion du colloque sur l'oeuvre d'Eugène ATGET qui s'est tenu au collège de France en juin 1985, nous avons étudié l'état de conservation ainsi que la nature des tirages effectués par le photographe pour les collections municipales parisiennes (1). Composé d'images positives *, ce fonds ATGET, d'environ 13000 épreuves, est surtout réparti entre le Musée Carnavalet et la Bibliothèque Historique de la Ville de Paris.

ATGET a photographié Paris et la région parisienne des années 1890 à 1927, date de sa mort. Cette époque, charnière pour l'histoire de la photographie, est celle d'une transition esthétique et d'une mutation technologique importante. La photographie quitte en effet progressivement le domaine artisanal et s'oriente vers l'industrialisation de produits prêts à l'emploi.

Si l'identification de la nature précise des matériaux photographiques permet d'établir une politique de conservation et de restauration adéquate, elle améliore également la compréhension et l'appréciation d'une oeuvre en éclairant les choix esthétiques du photographe en fonction des possibilités techniques de l'époque.

A la suite d'un examen visuel de l'ensemble de la collection, et à la demande du conservateur, il a paru nécessaire de faire appel à des méthodes d'analyse complémentaires. Nous avons donc cherché à appliquer à la photographie des techniques utilisées dans des domaines plus traditionnels de la conservation des oeuvres d'art. Cela, grâce à une collaboration avec le Laboratoire de Recherche des Musées de France pour l'étude des couches sensibles et du Centre de Recherche sur la Conservation des Documents Graphiques pour celle des supports.

1 - L'examen préliminaire

Trois groupes de procédés photographiques distincts, tous à noircissement direct **, ont été recensés dans le fonds ATGET :

1.1 Les épreuves albuminées

Leur identification visuelle sous loupe binoculaire ne pose aucun problème majeur (3). Elles forment la grande majorité des tirages d'ATGET et, à notre connaissance, ce sont les seules à avoir été utilisées par lui jusque dans les années 1920. Les premiers papiers pré-albuminés furent commercialisés autour de 1860. A partir de 1880 jusqu'en 1920 (période qui couvre la majeure partie de l'activité photographique d'ATGET) il devient possible d'acheter des papiers albuminés pré-sensibilisés. Ceux-ci restaient sensibles quelques jours grâce à l'addition d'acide citrique dans le bain de nitrate d'argent. ATGET a parfois employé des papiers teintés à l'aniline, comme l'attestent la coloration rosée de certains bords d'images qui ont été protégés de la lumière ou la présence d'une teinte chamois caractéristique dans les basses densités ***. Si la plupart des virages effectués par ATGET fournissent des tons bruns chauds plus ou moins altérés mais classiques des images albuminées, de très nombreux tirages, plus tardifs, tirent vers le pourpre noir ou même le gris.

Les supports de ces images semblent être des papiers de la Société Blanchet Frères et Kléber (B.F.K.) de Rives dont le filigrane apparaît sur certains tirages. Ces papiers sont encollés à l'amidon et à la résine (5).

Beaucoup d'épreuves albuminées d'ATGET ont des traces d'encaustique ou de vernis en surface. Si cette couche peut augmenter la brillance et la protection des images, elle a l'inconvénient de se salir et de jaunir en vieillissant. Les épreuves albuminées les plus altérées sont, en général, les plus anciennes ou celles qui sont contrecollées sur des cartons de mauvaise qualité.

* Quelques négatifs 18 x 24 sur verre subsistent néanmoins au Musée Carnavalet. La plupart des négatifs sont conservés aux Archives photographiques de la Direction du Patrimoine ou au Musée d'Art Moderne de la Ville de New-York.

** Les tirages à noircissement direct s'obtiennent par contact avec le négatif. Ils ont donc le même format que ce dernier (18x24 dans le cas d'ATGET). Leur mode de formation détermine les caractéristiques physico-chimiques des grains d'argent et donc, des images (2).

*** L'aniline, colorant très fugitif à la lumière, fut parfois employé par les fabricants à partir des années 1870 afin de contrecarrer le jaunissement naturel de l'albumine (4).



Epreuve mate à l'albumine



-Epreuve au gélatino-chlorure d'argent

STRATIGRAPHIE PAR COUCHE
ÉPAISSE (X 176)

Epreuve albuminée

1.2 Les tirages mats à noircissement direct

A une époque plus tardive (à partir de 1923) Eugène ATGET a employé des papiers esthétiquement très différents des papiers albuminés brillants. Il s'agit de tirages mats, obtenus sur papiers plus épais *, et sans couche de protection en surface comme l'attestent les nombreuses marques d'abrasion. L'examen sous loupe binoculaire permet de les assimiler à des papiers salés mais ils possèdent des tonalités peu usuelles pour ces derniers (du brun noir au gris violacé). S'il s'agissait bien de tirages argentiques, comme l'indiquait l'affaiblissement de certaines images, la nature exacte des encollages additionnels et des virages étaient problématique. En effet, resurgissant avec la mode des papiers mats au tournant du siècle, de nombreuses variantes de papiers salés à encollage additionnel apparaissent sur le marché. Les liants les plus fréquemment employés sont à base d'amidon (arrow-root), de résine, de caséine, d'albumine diluée, seuls ou en mélange. Par ailleurs, les virages aux sels de platine utilisés sur les papiers argentiques à partir de la fin des années 1880 peuvent procurer aux images des tonalités très noires, et furent appliqués aux papiers salés de cette époque.

1.3 Les émulsions au chlorure d'argent

Bien que commercialisées dès la fin du 19^e siècle, elles n'apparaissent à notre connaissance dans l'œuvre d'ATGET qu'à la même période que ses papiers mats. Fabriquées en usine, les émulsions à noircissement direct se caractérisent par la présence d'une couche de sulfate de baryum qui augmente la brillance et la blancheur de l'image. Celle-ci masque à l'examen sous loupe binoculaire les fibres du support. Ces premières émulsions souvent appelées "aristotypes" étaient composées de collodion ou de gélatine. L'identification de la gélatine a été faite par test ponctuel à l'eau, bien que les réactions aient parfois été atténuées par la couche d'encaustique en surface. De nombreux tirages sont mal conservés et une décoloration jaune caractéristique indique alors des traitements de fabrication défectueux, courants sur ce type de procédé photographique**.

2 - L'analyse des couches sensibles

En fonction des possibilités offertes, nous avons choisi de prélever dans les marges d'une trentaine *** d'épreuves, non montées sur carton, des échantillons de 1mm² environ qui ont servi à l'ensemble de l'expérimentation menée au Laboratoire de Recherche des Musées de France.

2.1. L'étude stratigraphique

Certaines caractéristiques techniques de la formation des images ainsi que les différences de structure correspondant aux trois procédés employés par ATGET ont été mis en évidence par l'observation de coupes transversales au microscope optique (x 176).

- Les épreuves albuminées :

L'image incluse dans la couche d'albumine reste en surface mais n'est pas séparée du papier de support.

- Les tirages mats à noircissement direct :

Comme dans le cas des papiers salés, la couche image pénètre dans les fibres du papier de support qui affleurent en surface.

- Les émulsions au chlorure d'argent :

Une mince couche de sulfate de baryum isole du support l'émulsion contenant l'image. La couche sensible est ici très fine par rapport aux deux autres procédés

2.2. L'analyse microchimique des liants et des émulsions

En prenant exemple sur les méthodes employées pour l'analyse des liants picturaux (7), nous avons d'abord essayé d'utiliser des coupes minces **** afin d'identifier la nature des constituants organiques des images par fixation de colorants spécifiques. Mais les échantillons ne pouvant être prélevés que dans les marges des épreuves, les coupes minces ont posé des problèmes pratiques. Les marges des images d'ATGET correspondent aux densités maximales, très chargées en argent et sont donc de coloration foncée. Celle-ci a gêné la lecture des réactifs colorés. Pour pallier à cet inconvénient il pourrait être envisagé, s'il est impossible de prélever dans des zones claires de l'image, de blanchir les couches argentiques par des traitements photographiques classiques. Il a semblé plus simple d'avoir recours à un autre moyen.

*Sur lesquels nous n'avons pas trouvé trace de filigrane.

** Si l'aspect en zones de certaines tâches chimiques indique une mauvaise agitation dans les bains, l'emploi combiné d'un bain virage-fixage conseillé par les fabricants à l'époque explique l'altération sévère de nombreux aristotypes.

*** Nous n'avons effectué que 7 prélèvements respectivement sur les papiers mats et sur les épreuves au gélatino-chlorure d'argent, alors que le double a pu être prélevé sur les images albuminées, plus nombreuses.

**** Les coupes minces ont l'avantage de ne requérir que très peu de matière; elles sont d'environ 50 microns d'épaisseur.

Des écailles de plus grande dimension ont été analysées directement au microscope optique. On a pu ainsi utiliser un échantillon témoin de référence sur une même lame afin de contrôler l'action des colorants spécifiques. Celle-ci est décrite dans divers articles (8), (9).

- Le noir amide 1, qui révèle la présence des protéines de l'oeuf, s'est bien fixé sur les épreuves albuminées.

Il a d'autre part permis d'identifier la présence d'albumine dans les tirages mats.

- Une solution aqueuse d'iodure de potassium et d'iode (lugol), colore l'amidon en violet. On a pu ainsi déterminer la présence d'amidon dans ces mêmes tirages. Ces papiers mats à l'albumine qui comprennent de l'albumine diluée et de l'amidon comme encollages additionnels sont vendus pré-sensibilisés dès 1899, et seront commercialisés jusqu'en 1929, sous diverses appellations *

La présence d'amidon dans les papiers de support a été d'autre part également vérifiée.

- Le noir amide 3 ainsi que la fuschine basique, qui colorent la gélatine, ont permis de contrôler la nature des émulsions au chlorure d'argent. La couche de sulfate de baryum imprégnée de gélatine se colore également, mais à un degré moindre. La couche d'encaustique a parfois gêné la lecture du test en masquant localement les réactions. Il faut alors tâcher de l'éliminer mécaniquement sous la loupe binoculaire.

Tirage mat à noircissement direct

2.3 L'analyse des éléments métalliques

La nature des virages effectués par ATGET a été contrôlée par microfluorescence X. La taille très réduite de nos échantillons n'a permis qu'une étude qualitative. Cette méthode non destructive dans son principe permet de réemployer les échantillons (11). Les résultats apparaissent sous forme de spectres dont la position des pics indique le niveau d'énergie caractéristique des éléments en présence. Toutes les images analysées, même les plus noires de tonalité ont été virées à l'or. C'est également le cas des papiers mats à l'albumine, qui étant noir-gris pouvaient ressembler à des tirages argentiques virés au platine. Dans le cas des virages à l'or, cette différence de tonalité est liée à la composition des bains (notamment au degré d'acidité) et au temps d'immersion. Les pics de baryum présents sur les spectres des papiers au gélatino-chlorure d'argent attestent la présence de la couche de sulfate de baryum (Cf. annexe).

3 - Etude microchimique de la composition fibreuse des papiers

Après défibrage et préparation des échantillons **, nous avons analysé les fibres des supports au Centre de Recherche sur la Conservation des Documents Graphiques. Les réactifs colorés (chloro-iodure de zinc et réactif de Lofton-Merritt) indiquent la nature des traitements de fabrication des pâtes (12); la morphologie des fibres permet de les identifier. Ces facteurs sont déterminants quant à la qualité des supports (13). En fonction du petit nombre d'échantillons *** nous n'avons pas effectué de tests sur la nature des encollages de Rives. Nous n'avons pu suivre l'évolution dans le temps de la qualité des fibres que dans le cas des épreuves albuminées; les autres, comme il a été dit, n'ayant été employées par ATGET que pendant une période très limitée.

3.1 Les papiers albuminés

Ces pâtes de très bonne qualité sont à base de chiffon (fibre de coton parfois mélangée au lin) et d'alfa (pâte chimique blanchie). Les traces de résineux relevées sur des papiers appartenant à des tirages de 1910 indiquent peut-être une légère évolution qualitative dans la fabrication des pâtes ****. Les fibres sont en général très courtes et fibrillées, indiquant des pâtes très raffinées qui fournissent des papiers compacts ayant une bonne résistance à l'eau.

3.2 Les papiers mats à l'albumine

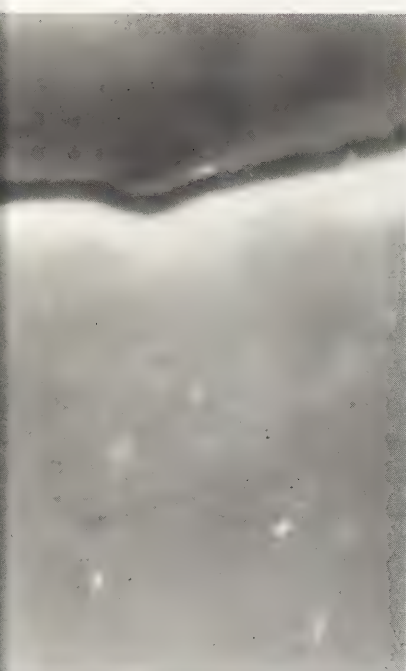
Leur composition fibreuse et le degré de raffinage des pâtes semblent très proches des papiers albuminés que nous avons analysés. La présence des résineux est ici attestée dans un cas seulement (n° 6466).

* Telles que papiers Alboidin, Albumon, Alumat, etc. (10)

** 13 papiers provenant des épreuves albuminées, 5 des épreuves mates à l'albumine et 5 de celles au gélatino-chlorure d'argent.

*** Celui-ci a également empêché d'effectuer une analyse quantitative de la nature des fibres.

**** L'alfa en mélange avec le coton est utilisé pour la fabrication des très beaux papiers. Les résineux fournissent des pâtes celluloses moins pures qui risquent dans certains cas de donner des papiers de moins bonne qualité.



Emulsion au chlorure d'argent

3.3 Les papiers au gélatino-chlorure d'argent

Un peu moins riches en pâtes de chiffon (coton, lin), les papiers analysés sont ici le produit d'un mélange plus équilibré avec les pâtes chimiques blanchies, au pourcentage plus réduit en cellulose. Celles-ci proviennent surtout des fibres de résineux et parfois de feuillus. L'historique des papiers de Rives(5) signale, en effet, l'introduction des feuillus dans la fabrication du papier gaslight "Artura" à partir de 1912. Les papiers "Cellodine" (au collodio-chlorure d'argent) et "Aristos" (au gélatino-chlorure d'argent) étant à l'époque encore fabriqués avec des pâtes 100% chiffon. Le pourcentage des pâtes de cellulose blanchie augmentera dans le temps et atteindra 100% vers 1932 dans le cas des papiers gaslight et bromure.

Si les papiers albuminés semblent qualitativement les meilleurs, il ne faut pas oublier que leur production s'éteint à partir de la fin de la première guerre mondiale. En 1923, leur prolongement commercial et leur substitut dans le cas d'ATGET, les papiers mats à l'albumine, imposent comme pour les papiers salés une excellente qualité du support directement au contact de l'image. Les papiers aristotypes, plus proches esthétiquement des épreuves albuminées brillantes en sont technologiquement très éloignés. Ils semblent appartenir, non seulement du point de vue structurel des couches sensibles mais également par la composition des papiers de support à une époque plus moderne. Ceux utilisés par ATGET dans les années 1920 possèdent néanmoins encore un pourcentage important de pâte de chiffon *. Cette différence dans la fabrication des papiers bien que réelle, paraît insuffisante pour avoir eu une influence sur l'altération des images.

NATURE DES FIBRES DES PAPIERS DE SUPPORT

PAPIERS ALBUMINES

n° du négatif : côte	date	COTON	LIN	ALFA	RESINEUX	FEUILLUS
100 b	: 1898	: X	:	: X	:	:
4647	: 1899	: X	:	: X	:	:
4582	: 1902	: X	:	: X	:	:
4868	: 1904	: X	:	: X	:	:
4869	: "	: X	:	: X	:	:
54	: 1910	: X	: X	:	:	:
707	: "	: X	:	: X	:	:
723	: "	: X	:	: X	: traces	:
725	: "	: X	:	: X	: traces	:
728	: "	: X	:	: X	: traces	:
442	: 1913	: X	: X	:	:	:
6438	: 1925	: X	: X	: X	:	:
6439	: "	: X	:	:	:	:

PAPIERS MATS A L'ALBUMINE

6436	: 1925	:	: X	: X	:	:
6457	: "	:	: X	: X	:	:
6466	: "	: X	:	:	: X	:
6469	: "	: X	: X	: X	:	:
6472	: "	: X	:	: X	:	:

PAPIERS AU GELATINO-CHLORURE D'ARGENT

6437	: 1925	: X	: X	:	: X	: X
6440	: "	: X	: traces	:	: X	:
6481	: "	: X	: traces	:	: X	:
6498	: "	: X	: traces	:	: X	: X
6499	: "	: X	: X	:	: traces	:

Bien que certaines difficultés pratiques aient été rencontrées, ces essais ont montré qu'il était possible d'obtenir des compléments d'information à l'examen visuel des photographies par des techniques d'analyse relativement simples à mettre en oeuvre. Grâce à ces méthodes, nous avons pu déterminer la nature pré-cise des papiers mats à l'albumine et démontrer qu'ATGET n'a employé tout au long de sa carrière que des virages à l'or, même sur des papiers très différents. Les supports matériels de ses images ont subi une évolution qualitative qui n'a néanmoins pas semblé poser de problème quant à leur stabilité. Par contre, l'opacité de certaines couches photographiques ainsi que la présence d'encaustique ont parfois gêné la lecture des tests microchimiques et la taille très réduite des prélèvements n'a pu permettre d'effectuer des analyses quantitatives réelles. Il serait donc intéressant de pouvoir comparer à l'avenir ces premiers résultats à ceux obtenus par des méthodes plus sophistiquées, plus précises et si possible, non destructives. La spectrométrie infrarouge à transformée de FOURIER pourrait avoir ces avantages et permettre une identification de toutes les substances en présence, organiques ou non, telles que encaustiques, vernis et couches photographiques opaques comprises.

* Et donc un taux élevé en cellulose.

REMERCIEMENTS

Je tiens à remercier pour leur collaboration :

- Sylvie COLINART et Alain DUVAL du Laboratoire de Recherche des Musées de France
- Françoise FLIEDER et Françoise LECLERC du Centre de Recherche sur la Conservation des Documents Graphiques

Je remercie également pour ses conseils préliminaires Siegfried REMPEL (Centre Canadien d'Architecture) et pour la mise en forme de ce manuscrit Sophie BRESOLIER (Atelier de Restauration des Photographies de la Ville de Paris).

BIBLIOGRAPHIE

- (1) Actes du colloque ATGET, collège de France, 14-15 juin 1985, dans "Photographies", numéro hors-série, mars 1986.
- (2) Nebelette's Handbook of photography and reprography, 7^e éd. Van Nostrand Reinhold, N.Y., 1977.
- (3) J. REILLY : Care and Identification of 19th century photographic prints Eastman Kodak Company, 1986
- (4) S. BURGI : Fading of dyes used for tinting unsensitized albumen paper "S.P.S.E. - International Symposium on the Stability and Preservation of photographic images" - Ottawa, 1982.
- (5) Les papeteries de Rives; imprimerie Allier, Grenoble 1950.
- Usines de Rives; document Arjomari, s.d.
- (6) Les méthodes scientifiques dans l'étude et la conservation des oeuvres d'art.
Laboratoire de Recherche des Musées de France - La Documentation Française, 1984.
- (7) M.C. GAY : Essais d'identification et de localisation des liants picturaux par des colorations spécifiques sur des coupes minces.
Annales du Laboratoire de Recherche des musées de France, 1970.
- (8) E. MARTIN : Contribution à l'analyse de liants mixtes.
Comité pour la Conservation de l'ICOM, 5^e réunion triennale, ZAGREB, 1978
- (9) E. MARTIN : Some improvements in techniques of analysis of paint media
Studies in Conservation, 22, 1977.
- (10) J. REILLY : The albumen and salted paper book
Light impressions, Rochester, 1980.
- (11) Ch. LAHANIER : Application des techniques de microfluorescence X au Laboratoire de Recherche des Musées de France
International Symposium of the Conservation and Restoration of Cultural Property, Tokyo, 1978.
- (12) L. VIDAL : L'analyse microscopique des papiers, Grenoble, 1939.
- (13) BROWNING (B.L.) : Analysis of paper, Marcel Dekka, New-York, 1969

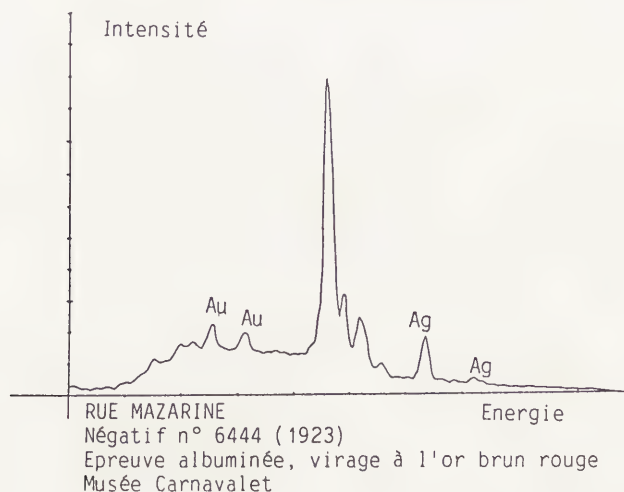
ANNEXE

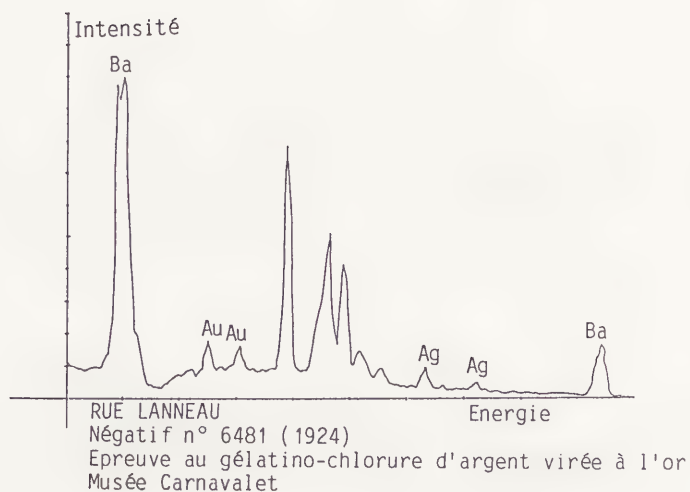
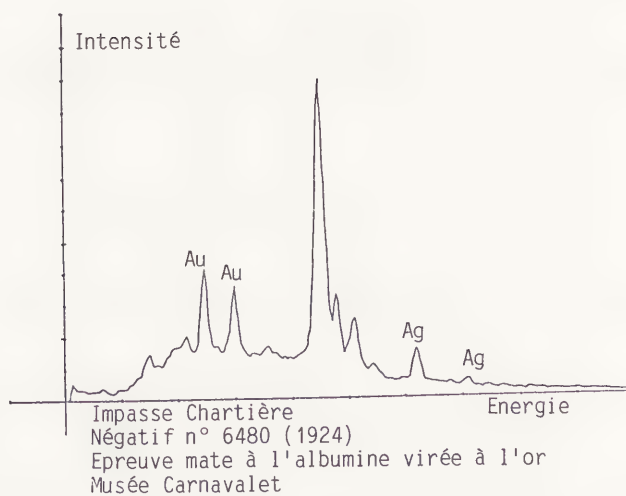
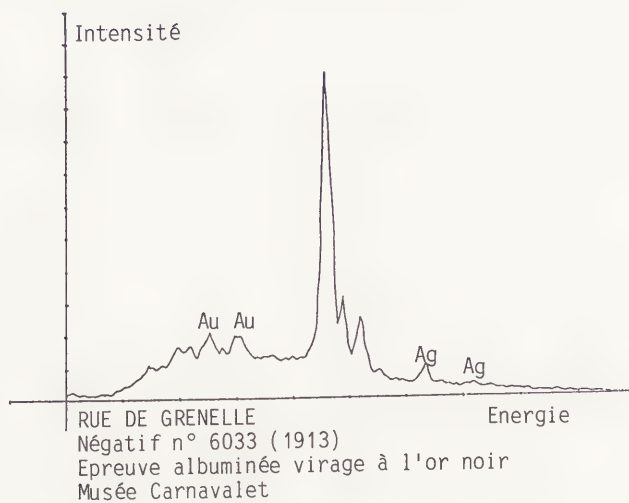
MISE EN EVIDENCE DU VIRAGE A L'OR PAR SPECTROMETRIE DE MICROFLUORESCENCE X

Au : Or (virage)

Ag : Argent (couche sensible)

BA : Baryum (couche intermédiaire de sulfate de baryum).





RESUME

Si plusieurs méthodes d'analyse peuvent être employées actuellement pour la détection d'éléments en trace dans un échantillon, le nombre de ces méthodes devient extrêmement réduit lorsqu'il s'agit d'analyses en termes de composés, c'est-à-dire aptes à détecter et à caractériser au sein d'un mélange la présence d'un composé en trace.

Les exemples qui sont présentés tentent d'illustrer les possibilités nouvelles offertes dans ce domaine par la spectrométrie Raman.

En mettant à profit plus particulièrement l'effet Raman de résonance et l'effet Raman exalté de surface, ces méthodes permettent désormais, grâce à leur très grande sensibilité, l'analyse de très faibles concentrations pouvant atteindre couramment 10^{-4} à 10^{-6} M.

IDENTIFICATION DE COLORANTS ORGANIQUES NATURELS PAR MICROSPECTROMETRIE RAMAN DE RESONANCE ET PAR EFFET RAMAN EXALTE DE SURFACE (S.E.R.S.) ;
Exemple d'application à l'étude de tranchefiles de reliures anciennes
teintes à la garance

Bernard GUINEAU : Centre de Recherches sur la Conservation des Documents Graphiques, 36 rue Geoffroy-Saint-Hilaire, 75005 PARIS - France
 Vincent GUICHARD : Laboratoire de Spectrochimie Infra Rouge et Raman du C.N.R.S., 2 rue Henry Dunant, 94320 THIAIS - France

L'identification précise de colorants organiques employés en peinture ou en teinture sur des oeuvres conservées (peintures de manuscrits médiévaux, textiles archéologiques, ...) se heurte encore à de nombreuses difficultés.

La première de ces difficultés réside principalement dans les très faibles quantités de colorant généralement disponibles : celui-ci ne représente, en effet, qu'une infime fraction du mélange d'autres composés organiques ou minéraux constitutifs du support sur lequel le colorant est adsorbé ou fixé. Les méthodes d'analyse susceptibles d'être employées avec quelque chance de succès, se doivent donc d'être suffisamment sensibles pour être aptes à détecter la présence d'un composé même à l'état de trace au sein d'un mélange. C'est ainsi que les mesures généralement réalisées en spectrométrie d'absorption infra rouge sans séparation des composants se révèlent peu satisfaisantes car les bandes d'absorption caractéristiques du colorant à identifier sont le plus souvent masquées par celles beaucoup plus intenses du support cellulosique, protéinique ou minéral sur lequel le colorant est fixé.

Une seconde difficulté réside dans la "fragilité" des composés que l'on cherche à identifier, fragilité due par exemple à leur très grande sensibilité photochimique. Nombreux sont en effet les colorants organiques d'origine naturelle qui s'altèrent soit au cours de leur vieillissement, soit sous l'effet d'une excitation provoquée pour les besoins de l'analyse. Ces risques d'altération sont encore augmentés dès lors que le colorant a été extrait et n'est donc plus fixé sur son support d'origine.

Enfin, toute méthode d'analyse ne peut être que comparative et s'appuie nécessairement sur un ensemble de données de référence. De telles données dans le domaine des colorants anciens sont souvent difficiles à réunir : certains des colorants utilisés autrefois nous sont encore mal connus, soit que leur désignation dans les textes historiques prête à confusion, soit que quelques-uns d'entre eux aient aujourd'hui, comme le Kermès, à peu près complètement disparu.

Les mesures nécessitent donc le recours à des méthodes très sensibles, capables d'analyser d'infimes fractions (quelques dizaines de picogrammes), telles que les techniques de microspectrométrie. En outre, les résultats obtenus devront toujours être interprétés en tenant compte de la transformation possible des composés en présence, notamment sous l'influence de l'éclairement. Pour tenter de surmonter ces difficultés, notre choix s'est porté plus particulièrement sur deux méthodes d'analyse : la spectrométrie Raman de résonance et la spectrométrie de fluorescence UV-Visible.

La fluorimétrie, basée sur la désexcitation des niveaux électroniques de la molécule est, comme on le sait, une méthode extrêmement sensible pour l'identification et le dosage de colorants organiques (la sensibilité de détection est en moyenne de l'ordre de 10^{-3} M à 10^{-5} M). Cette méthode, cependant, est encore peu utilisable en tant que telle pour la caractérisation des composés, à partir par exemple d'un profil d'excitation de fluorescence, mais de larges perspectives sont ouvertes actuellement dans ce domaine. En outre, certaines mesures portant sur des matériaux archéologiques plus ou moins altérés ou contaminés par l'environnement dans lequel ils ont pu être conservés, sont difficilement reproductibles.

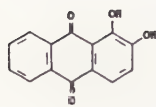
L'effet Raman de résonance permet en revanche de caractériser des colorants organiques, de façon plus précise grâce à l'observation de certains modes de vibration de molécule excités en résonance au voisinage d'une transition électronique. Cette technique permet de bénéficier d'une sensibilité accrue grâce à une forte augmentation de la section efficace de diffusion pour les modes de vibration considérés (sensibilité qui n'égale cependant pas celle de la fluorimétrie).

Un effet similaire a été décrit depuis quelques années pour des molécules adsorbées sur des surfaces métalliques convenablement préparées ; il s'agit de l'effet Raman exalté de surface (S.E.R.S.) dont l'interprétation est encore discutée.

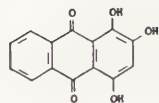
Nous présentons ici quelques exemples d'application portant sur les composés de la garance et mettant à profit cet effet de résonance ainsi que quelques résultats préliminaires exploitant l'effet Raman exalté de surface (S.E.R.S.).

I - Mesures "in situ" de laques et de teintures de garance par microspectrométrie Raman de résonance

Rappelons que la garance, généralement utilisée sous forme de laque ou de colorant mordancé fournit toute une gamme de teintes rouges, brun-rouge et orangées. Ce colorant d'origine naturelle est composé essentiellement de deux dérivés anthraquinoniques : l'alizarine (I) et la purpurine (II), le premier étant le composé majoritaire.



(I)



(II)

Pour ce composé, la présence d'une bande d'absorption dans le domaine visible, de longueur d'onde accessible avec les lasers couramment utilisés en spectrométrie, permet de tirer parti de l'effet Raman de résonance : certains modes de vibrations de la molécule (ceux qui assistent le changement de géométrie accompagnant la transition électronique) sont exaltés lorsque la longueur d'onde de l'excitation se situe dans la bande d'absorption ou au voisinage de cette bande. L'exploitation de ce phénomène reste cependant souvent limitée car l'irradiation dans de telles conditions conduit également au phénomène de fluorescence maximum qui entre alors en compétition avec l'effet Raman de résonance. Le rendement de fluorescence est supérieur de plusieurs ordres de grandeur à celui de la diffusion Raman et peut ainsi le masquer totalement. L'examen "in situ" de ces colorants risque donc d'être fortement gêné, comme le montrent les exemples suivants.

La figure 1B présente un spectre Raman relevé "in situ" avec la microsonde Raman sur un brin de laine teint à la garance. On observe que seules les trois raies les plus intenses de l'alizarine sont discernables : raies à 1282 cm^{-1} , 1327 cm^{-1} , 1475 cm^{-1} . A ces raies se superpose un important fond de fluorescence qui ne peut être diminué même en utilisant des temps d'intégration assez longs. En outre, le fait que l'on n'attende pas d'effet de résonance pour le support (kératine) à la longueur d'onde utilisée, explique que l'on n'observe aucune autre raie Raman; celles-ci, étant de faible intensité, sont masquées par la fluorescence.

La figure 1C montre les mesures réalisées "in situ" d'une manière semblable sur une laque de garance. On observe sur le spectre le même ensemble de raies Raman auquel se superpose un fond de fluorescence encore plus intense. Ces spectres peuvent être comparés à celui relevé pour un échantillon de référence d'alizarine (figure 1A).

On voit ainsi les limites de la méthode, le rapport signal sur bruit des mesures étant relativement faible, en dépit de l'emploi de constantes de temps assez élevées pour l'enregistrement. Ce rapport signal sur bruit ne peut être amélioré par l'utilisation de puissances d'irradiation plus élevées sans risque d'altérer les composés en présence.

II - Mesures sur le colorant extrait

Comme l'analyse des colorants "in situ" est pour le moins difficile, voire parfois impossible, nous avons été amenés à exécuter un traitement préalable des échantillons afin de tenter de reconcentrer le colorant dispersé au sein du support. Nous avons utilisé les procédés d'extraction classiques, couramment utilisés, notamment pour les mesures chromatographiques.

Il s'avère impossible, cependant d'obtenir un spectre Raman des solutions ainsi préparées, en raison d'une très rapide photo-dégradation des colorants dans ces conditions.

En revanche, il a été possible de relever des spectres significatifs à partir de dépôts extrêmement localisés réalisés avec ces solutions sur des plaques en gel de silice semblables à celles utilisées en C.C.M. La difficulté, dans ce cas, étant de réaliser un dépôt suffisamment concentré à partir d'une solution de quelques dizaines de microlitres. Cette difficulté a pu être surmontée, cependant, grâce à l'emploi d'une seringue (applicatrice) qui permet des applications répétées au même point sans risque d'accident (détérioration du gel, élargissement du spot, ...). Nous en montrerons un exemple.

Application à l'étude des tranches de manuscrits médiévaux

Nous avons entrepris la mise en œuvre de ces différentes procédures d'analyse (extraction et mesures en microspectrométrie Raman) sur quelques tranches de manuscrits médiévaux. Ces tranches qui sont remplacées à l'occasion de la restauration des reliures, constituent un matériel relativement abondant. Leur étude apporte une information supplémentaire sur les techniques employées à certaines époques et donne de précieuses indications sur les colorants susceptibles d'avoir été utilisés pour l'ornementation des manuscrits eux-mêmes.

L'exemple qui est présenté ici se rapporte à une tranche provenant de la reliure d'un Coran du XIII^e siècle. Les analyses ont porté sur les fils teints en rouge. A partir d'un brin de quelques millimètres de longueur, l'extraction du colorant a été faite en ampoule scellée à 80°C , dans un mélange d'acide chlorhydrique à 5 % et d'acétone (1/1). La solution a été ensuite évaporée sous vide, puis reprise avec 20 microlitres de méthanol avant d'être déposée ponctuellement et évaporée sur un support en gel de silice d'un type utilisé pour la chromatographie en couche mince.

Au cours de l'évaporation du solvant se forment de fines cristallites de quelques microns de longueur sur lesquelles se font directement les mesures Raman.

Le spectre obtenu (figure 2B) permet d'identifier sans ambiguïté la présence de garance comme le montre sa comparaison avec le spectre d'un échantillon de référence d'alizarine, le composé principal de ce colorant (figure 2A).

Les plus grandes précautions doivent être prises cependant dans le choix des paramètres expérimentaux, à cause de la fragilité des composés analysés (dégradation par réaction photochimique). La destruction du matériau survient d'autant plus vite que le laser est focalisé sur une surface de l'ordre du μm^2 qui reçoit donc une irradiance très élevée. La puissance du laser utilisée doit donc être aussi réduite que possible. L'ordre de grandeur de cette puissance à la sortie du laser est de 10 mW, encore la réduit-on en interposant des filtres de densité entre la source et l'entrée du spectromètre. Avec un filtre ne laissant passer que 10 % de la puissance et en tenant compte des pertes dues à l'optique de transfert (filtre interférentiel, microscope ...) la puissance sur l'échantillon n'excède pas 100 μW .

Il paraît illusoire, enfin, de vouloir fixer un seuil de détectivité pour les colorants que nous avons pu étudier par cette méthode. S'il est effectivement possible d'obtenir un spectre identifiable sur une cristallite de quelques microns de longueur (soit une masse de l'ordre du picogramme), la limite tient plus à la quantité minimale d'échantillon que l'on peut manipuler qu'à la sensibilité des moyens spectrométriques mis en œuvre.

III - Mesures par spectrométrie Raman S.E.R.S. sur le colorant extrait

En dernier lieu, nous avons tenté de tirer profit de l'effet Raman exalté de surface plus connu sous le nom de S.E.R.S. (Surface Enhanced Raman Scattering), phénomène mis en évidence voici une dizaine d'années.

Cet effet se traduit par l'exaltation du signal Raman de plusieurs ordres de grandeur (pouvant atteindre des facteurs de 10^6 à 10^{10}) lorsque certains composés sont adsorbés sur un métal noble possédant une surface rugueuse.

Malgré de très nombreux travaux (1), l'effet SERS n'a pu être encore clairement interprété ; il semble faire intervenir à la fois un phénomène purement électromagnétique dû aux propriétés optiques de la surface métallique et des interactions spécifiques entre l'adsorbat et la surface dont l'effet est de rendre possible des transferts d'énergie très efficaces entre le métal et cet adsorbat.

Le point qui nous intéresse ici est que cet effet SERS est particulièrement important pour de nombreux composés aromatiques. C'est ainsi que quelques composés colorés ont déjà fait l'objet d'études en SERS, mais ces travaux sont encore le plus souvent limités à des démonstrations de faisabilité et portent rarement sur des applications analytiques. Notons, enfin, que l'effet SERS s'accompagne d'une baisse notable des rendements de fluorescence observés pour les composés adsorbés ce qui renforce encore son intérêt pour l'application à l'étude de colorants très fluorescents comme le sont les composés anthraquinoniques.

Un des moyens habituellement utilisés pour obtenir les surfaces métalliques souhaitées consiste en un traitement électrochimique approprié obtenu, par exemple, par oxydation d'une électrode d'argent dans une solution aqueuse de bromure de potassium. Cette oxydation conduit à la formation en surface d'un dépôt de bromure d'argent, transformé ensuite par réduction en une couche poreuse d'argent. On introduit habituellement ensuite le composé à étudier dans la cuve à électrolyse et l'acquisition du signal Raman se fait alors directement "in situ" sur l'électrode.

Pour éviter cependant toute complication due à la réactivité du colorant (les anthraquinones sont en effet facilement réduits), et s'affranchir des problèmes de solubilité (peu de colorants sont en effet hydrosolubles), nous avons choisi de faire un traitement préalable de l'électrode sur laquelle une fois sortie de la cuve à électrolyse, une goutte de solution du colorant a été déposée puis séchée. Enfin, pour plus de sécurité, les mesures ont été effectuées sur l'électrode maintenue à 77 K, dans un cryostat à azote liquide pour éviter tout risque de dégradation de l'échantillon soumis à l'irradiation Laser.

Les mesures montrent que l'alizarine, sous forme anionique, présente effectivement un fort signal SERS (figures 4A et 4B). Les spectres Raman obtenus montrent ainsi un bien meilleur rapport signal sur bruit qu'en spectrométrie Raman classique. Il convient, cependant, de tenir compte de règles de sélection différentes de celles de la spectrométrie Raman conventionnelle ; ces règles qui dépendent sans doute de la géométrie d'adsorption, laquelle ne peut être parfaitement contrôlée, sont probablement à l'origine de certaines différences observées sur les spectres (variations d'intensité de certaines raies Raman) lesquels ne sont pas toujours parfaitement reproductibles. Il n'en reste pas moins que les mesures réalisées permettent d'identifier sans ambiguïté la présence d'alizarine par un ensemble de raies apparaissant à fréquences fixes et dont seulement quelques-unes peuvent varier d'une façon sensible en intensité, selon les conditions expérimentales.

La figure 3B montre le spectre SERS de la garance extraite d'un brin de laine teinte. Cet extrait a été obtenu à partir d'un poil d'une dizaine de microns d'épaisseur et d'une longueur de quelques millimètres. Les mesures montrent la présence de nombreuses raies communes avec celles de l'alizarine ainsi que quelques raies de fréquences différentes pouvant être attribuées à la présence de purpurine.

Cette étude préliminaire montre que le SERS peut devenir une technique d'analyse précieuse pour l'identification de colorants d'intérêt archéologique en raison de son extrême sensibilité qui autorise l'étude d'échantillons de taille très réduite, tout en apportant des résultats très complémentaires à ceux d'autres techniques d'analyse.

IV. Conclusion

Les mesures en spectrométrie Raman, quelle que soit la configuration utilisée, restent d'une mise en œuvre délicate pour l'étude de colorants en faibles fractions et néanmoins fortement fluorescents. Cette spectrométrie offre cependant des perspectives intéressantes. Dans le cas de colorants organiques, toujours très dilués, parfois partiellement altérés, la spectrométrie Raman reste l'un des seuls recours possibles. Les mesures Raman permettent en effet d'observer sélectivement ces composés même lorsqu'ils ne sont présents qu'en très faibles quantités. La méthode pourrait dans l'avenir être plus fréquemment exploitée, notamment lorsqu'on maîtrisera mieux les techniques de préparation des échantillons les mieux adaptées aux mesures.

Conditions expérimentales

L'alizarine étudiée est un produit de synthèse PROLABO, utilisé après purification par recristallisation à partir de méthanol.

Les échantillons de laine teinte ont été préparés par le Centraal Laboratorium voor Onderzoek van voorwerpen van kunst en wetenschap d'Amsterdam. Les tranchefiles de reliures anciennes ont été aimablement mises à notre disposition par le Département des manuscrits et par le Service de Restauration de la Bibliothèque Nationale. Les mesures Raman "in situ" ont été effectuées avec la microsonde Raman MOLE de JOBIN-YVON, et la microsonde à détection multicanale "MICRODIL 28" de DIOR. Les mesures des composés en solution et les mesures SERS ont été réalisées sur un spectromètre Raman conventionnel CODERG T 800, la surface des électrodes étant placée à 45° du faisceau incident et le faisceau diffusé collecté à 90° du faisceau incident.

Le traitement chimique est obtenu dans une solution aqueuse (eau bidistillée) de KBr à 0,1 M, en utilisant une contre électrode de platine et une électrode de référence au calomel saturé, l'électrode d'argent étant au préalable nettoyée avec un mélange d'acide chloro-chromique puis à l'ammoniaque avant d'être polie à l'aide de poudre d'oxyde de cérium.

Bibliographie

(1) Surface Enhanced Raman Scattering R. R. CHANCE and T.E. FURTAK Editor, New York, 1982

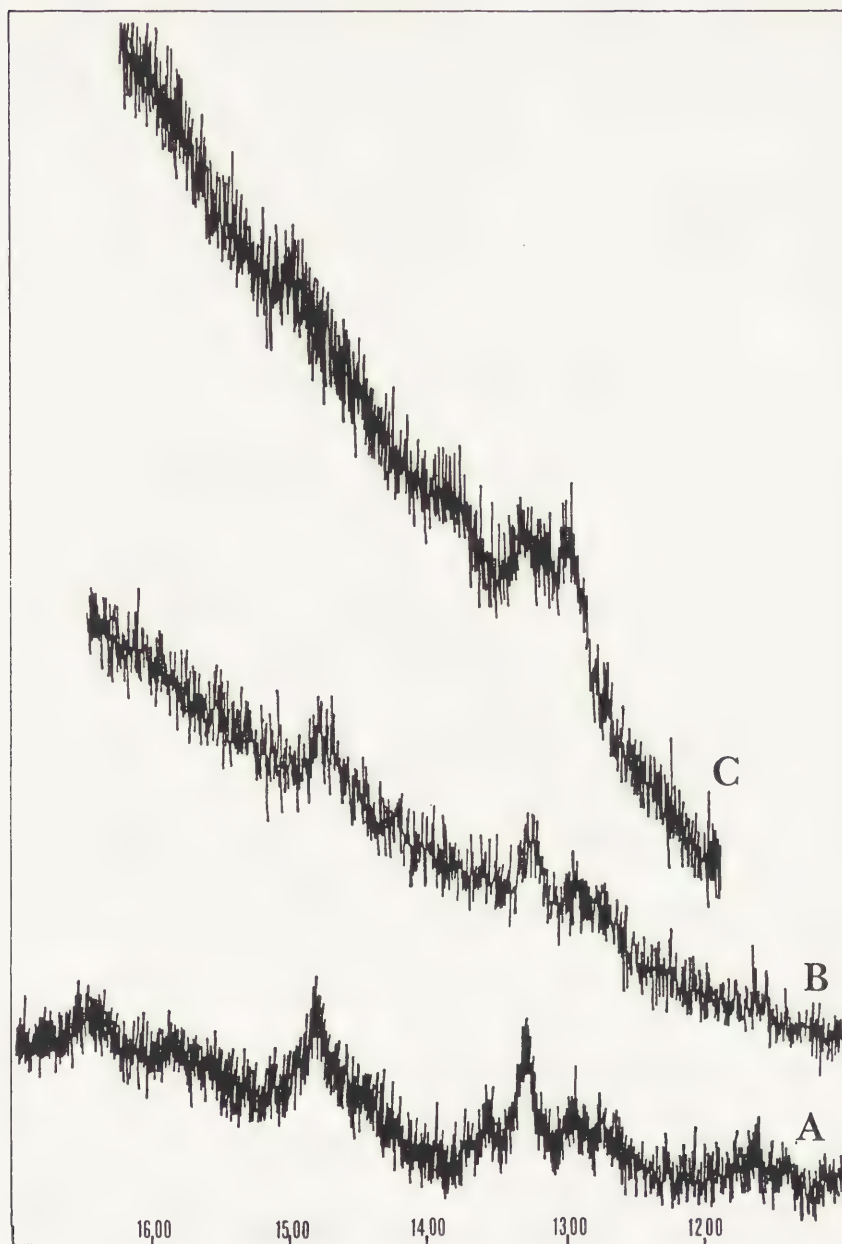


Figure 1 : spectres obtenus in-situ avec la microsonde Raman

- A - échantillon de référence d'alizarine
- B - échantillon de laine teinte à la garance
- C - échantillon de laque de garance

($\lambda = 457,9\text{nm}$; fente spectrale 10 cm^{-1} ; puissance laser 5 mW , temps d'acquisition 70 mn
objectif $100\times$)

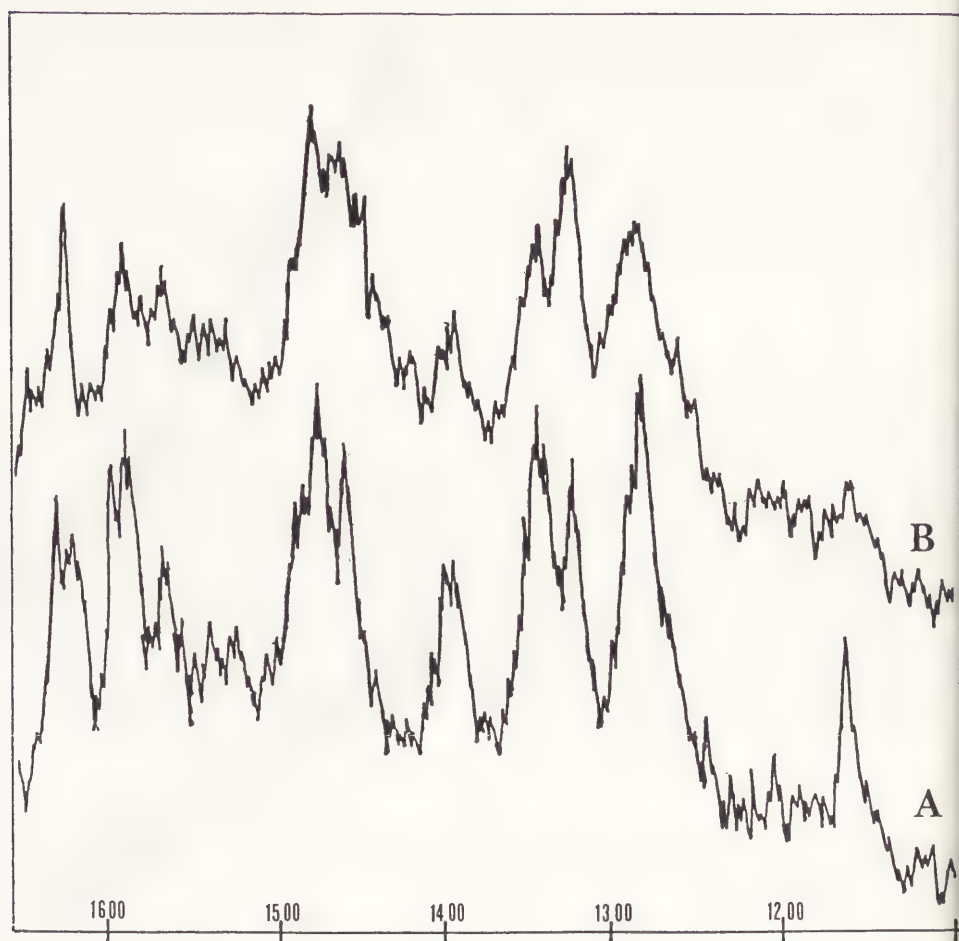


Figure 2 : spectres Raman obtenus sur des dépôts sur plaque de silice, avec la microsonde Raman multicanal

A - échantillon de référence d'alizarine

B - colorant rouge extrait d'une tranche de la reliure d'un Coran du XIII^e s.

($\lambda = 457,9\text{nm}$; puissance laser 0,5 m W ; temps d'acquisition 25 mn ; objectif 100 x)

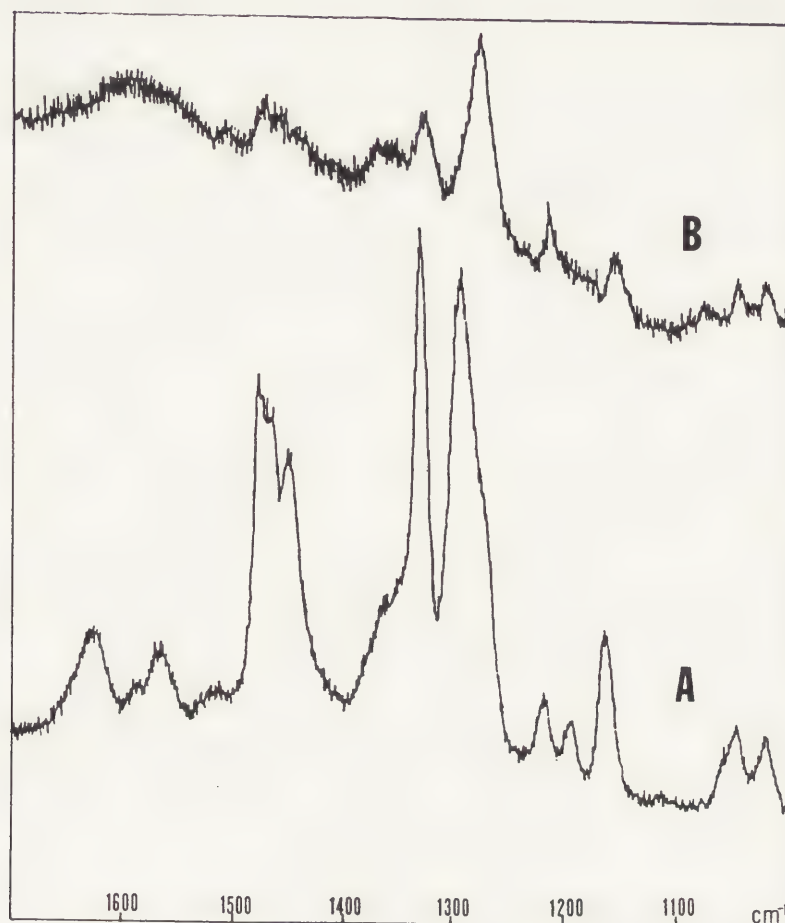


Figure 3 : spectres de SERS sur électrode d'argent

A - échantillon de référence d'alizarine

B - colorant extrait d'un brin de laine moderne teint à la garance

($\lambda = 514,5\text{nm}$; puissance laser 12 m W pour A, 20 m W pour B ; fente spectrale 4 cm^{-1} pour A, 7 cm^{-1} pour B ; temps d'acquisition 11 mn)

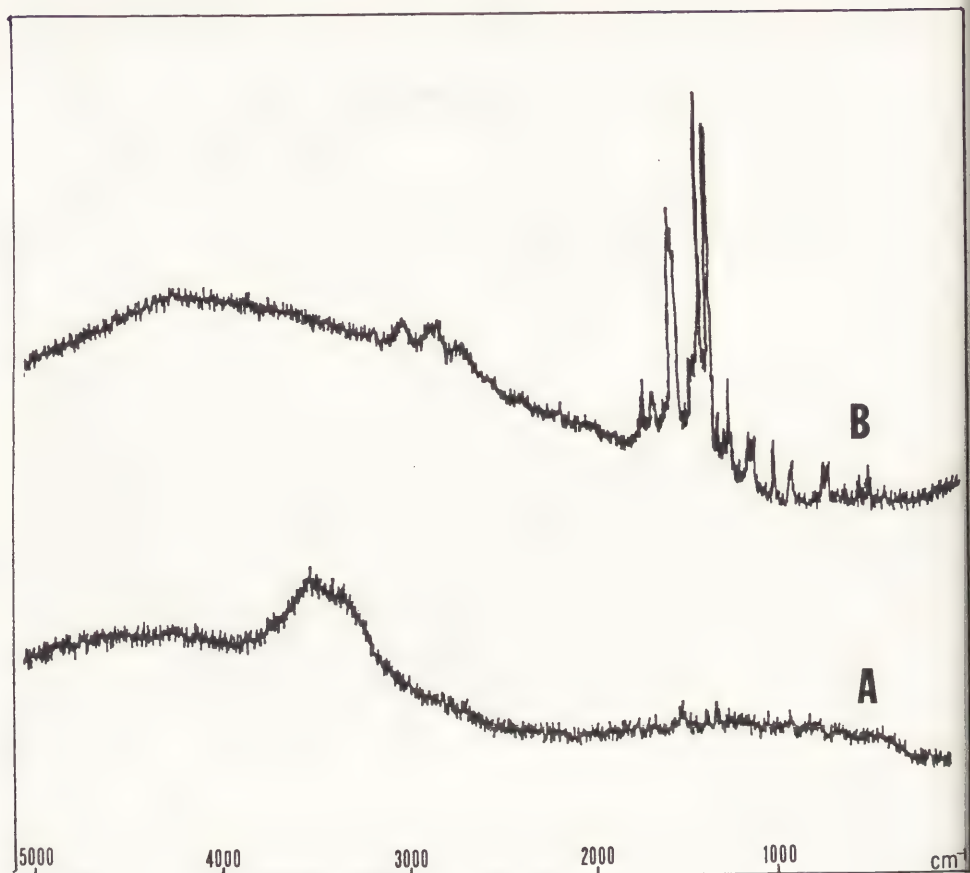


Figure 4 : spectres de diffusion de l'alizarine sous excitation à 514,5nm

- A - solution aqueuse légèrement caustique de concentration $2 \times 10^{-5} \text{ M}$ (puissance laser 55 mW ; fente spectrale 4 cm^{-1} ; temps d'acquisition 20 mn) - la bande large centrée à 3350 cm^{-1} est due au signal Raman de l'eau
- B - spectre de SERS d'une goutte de la même solution (puissance laser 12 mW ; fente spectrale 4 cm^{-1} ; temps d'acquisition 20 mn).

SUMMARY

Methods for the evaluation of treatments for discolored black-and-white films and papers in chemical solutions have been further refined. The morphology of silver grains in untreated and variously treated black-and-white prints and films has been recorded and examined closely. Transmission electron micrographs of particles of image silver demonstrate that chemical treatments of black-and-white images do not result in a weakened or deteriorated grain structure. Rather, it can be demonstrated that the final step in the proposed restoration procedure, which consists of selenium toning, leads to a more stable black-and-white image that is unlikely to deteriorate chemically again in its future life. These conclusions are confirmed by the results of accelerated aging tests.

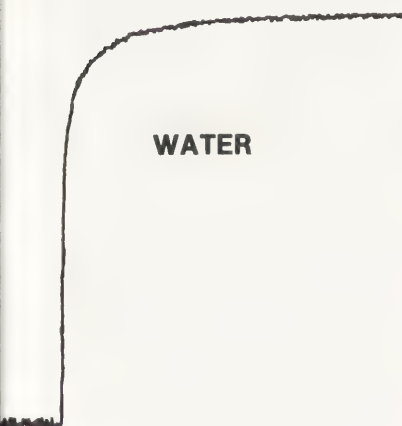


Figure 1: The swelling in water of the gelatin layer in a black-and-white film.

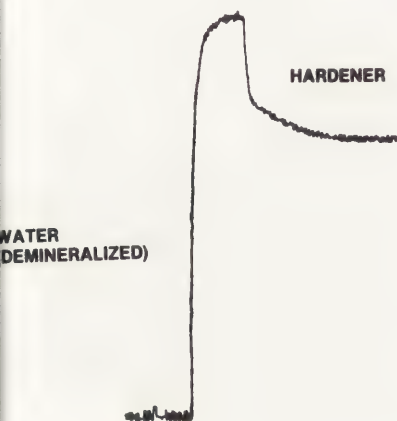


Figure 2: The effect of a hardener on the swelling of the gelatin layer.

FURTHER EXPERIMENTS ON THE RESTORATION OF DISCOLORED BLACK-AND-WHITE PHOTOGRAPHIC IMAGES IN CHEMICAL SOLUTIONS

Klaus B. Hendriks and Lincoln Ross

Picture Conservation Division
Public Archives of Canada
395 Wellington Street
Ottawa, Ontario
K1A 0N3
Canada

Chemical treatments of discolored films or papers continue to be of an experimental nature, while presenting at the same time a tremendous challenge. Such treatments are indigenous to photographic materials, since similar procedures have not been described for any other types of images such as watercolors, oil paintings, and so on. The destruction of dyes in color photographic materials by either hydrolytic reactions, by photo oxidation, or by chemical reductions is considered to be irreversible. The discoloration of black-and-white images, however, is generally due to a mechanism that is well understood at this point, leading to oxidized silver in the form of silver salts. The aim of chemical treatments of the kind described here is to convert such silver salts back to black elemental image silver.

Chemical treatments of stained or discolored black-and-white images can be classified into various categories. Traditional ways of improving photographic negatives include such procedures known as intensification or reduction. In these treatments image silver is either removed or image silver is added from the solution. In one treatment of intensification image silver is converted into silver compounds that have a higher density than that displayed by the original image silver. At any rate, in both of these treatments, image-forming substance is either added or removed, as the name reduction/intensification already indicates. Similarly, in treatments designed to remove the blue metallic sheen on the surface of certain black-and-white photographs, also known as silver mirroring, image silver is actually removed from the surface of the picture. This can either be done with an acidic ammonia hypo reducer, or it can be done with a solution of iodine in anhydrous alcohol, and with some other treatments. The methods discussed here, about which we have reported earlier (1), are of a different nature. No image silver is added, and no image silver is removed during the process. They are not intensification reactions. The treatment relies on the combined amount of image silver and silver salts still present in the original picture.

The principle of this method consists of converting a mixture of image silver and silver salts as deterioration products uniformly back into a silver halide. The silver halide is now developable, that is it can be uniformly and consistently converted back to black image silver. The conversion of image silver and silver salts into a silver halide is known as the bleaching step. In a second treatment, these silver halides are now uniformly treated with a photographic developer or a blackening agent, which is chemically a reducing compound, and so converted back into image silver.

A number of criteria must be met in order to make such a treatment successful. The quality of any photographic image is determined by its characteristic curve, its granularity and its sharpness. The purpose of this presentation is to demonstrate that in our treatment it is possible to maintain the integrity of the characteristic curve of the treated image. We also intend to demonstrate that the granularity of the restored image is equal to that of the untreated image. Furthermore, we intend to demonstrate our ability to control the stability of the gelatin layer on the treated films and papers, an important factor as the pictures pass through a series of chemical solutions ranging from a highly acidic bleaching solution to a strongly alkaline developing bath. This exerts tremendous pressure on the gelatin layer which can be demonstrated by its swelling and deswelling as it passes through the various chemical solutions that comprise the proposed treatment. The swelling of the gelatin layer indicates a simultaneous weakening of its structure. In other words, the more the gelatin layer swells the more it takes up water and the weaker it becomes, and the nearer it reaches the break-up point. However, we have succeeded in controlling the swelling by adding photographic hardeners at strategic intervals during the procedure. The effect of these hardeners can be demonstrated by measuring and recording the swelling and deswelling of the gelatin layers as the print or film passes through the treatment solutions. The third objective of this study was to examine the morphology of the elementary particles of image silver before and after the chemical restoration treatment. It is the size and shape and distribution of these image particles which determine to a large degree the image properties.

Figure 1 shows swelling of the gelatin layer in an aqueous solution: in pure water the gelatin swells to a finite value. Figure 2 shows the effect of the addition of a hardener on the swelling of the gelatin layer: it is decreased rapidly as soon as a chemical hardener has been added. Figure 3 shows the swell curve of a gelatin layer as it passes through the whole sequence of chemical treatments. In our observation, the crucial point was the final development



Figure 4: Transmission electron micrograph of processed silver grains from Eastman Kodak Velox Paper. (All electron micrographs at a magnification of 60,000X.)



Figure 5: Transmission electron micrograph of silver grains from previous paper after treatment in experimental restoration sequence.

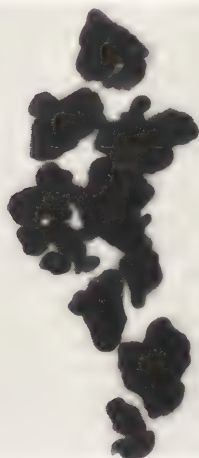


Figure 6: Transmission electron micrograph of silver grains from previous print after experimental restoration procedure and treatment in Selenium toner.

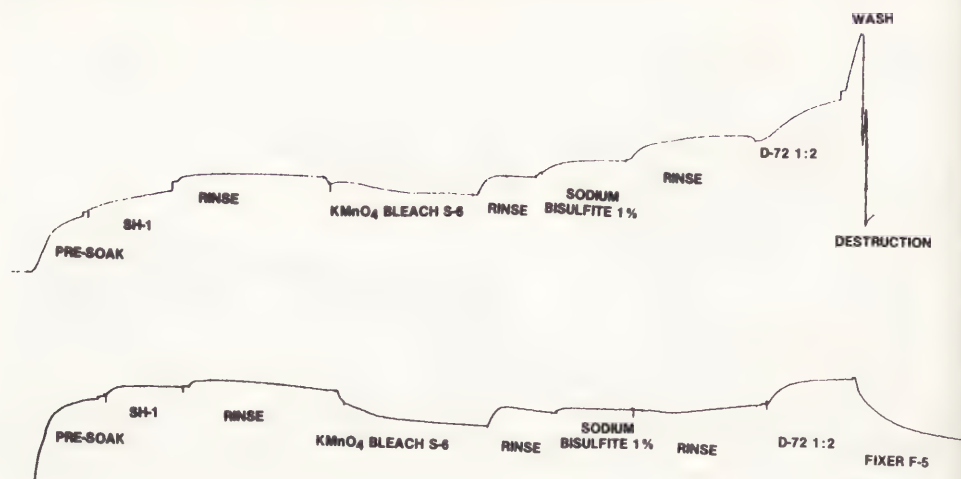


Figure 3: Effect of a hardening fixer on the swelling of the gelatin layer in a print after redevelopment.

step followed by an aqueous wash. We have replaced the water wash with a treatment in an acid hardening fixing bath, and so succeeded in controlling excessive swelling of the gelatin layer and keeping the print intact. This can clearly be seen in Figure 3. In order to assess the fate of the individual image particles, their morphology was studied by transmission electron microscopy (TEM).

TEM was first used by von Ardenne almost fifty years ago to study the size and shape of processed silver grains (2). Hall and Schoen (3), and Mees (4) demonstrated the usefulness of this new analytical tool for the study of the formation of silver during development, which expanded our understanding of the photographic process. Numerous publications have followed these pioneering studies. Blake and Meerkamper (5), Koerber (6), and Weyde (7) have published useful summaries that elaborate on the relationship between the morphology of processed silver grains and virtually all relevant image properties.

Figure 4 shows an electron micrograph of an undeteriorated contemporary black-and-white print made on Eastman Kodak Velox Paper. Figure 5 shows an electron micrograph of silver grains from the same print after it has undergone chemical treatments in our proposed reaction sequence. It can clearly be seen that the morphology of the original silver grains has been changed and the silver grains now appear to be smaller than previously. When, however, the chemically treated silver grains are toned in a selenium bath, the structure of the silver grain becomes consolidated. This is presented in Figure 6 which shows an electron micrograph of a selenium toned silver grain that previously has undergone treatment in our restoration procedure. Figures 7 to 9 show a similar sequence of transmission electron micrographs of silver grains from Eastman Kodak Kodabromide Paper.

During our presentation, we shall show a series of characteristic curves of print materials treated before and after treatment; a series of swell curves demonstrating the effectiveness of intermittent additions of hardeners in order to control the stability of the gelatin layer; and we will present transmission electron micrographs of a variety of silver grains from different products before and after treatment demonstrating that if the sequence is carried out properly and includes a final toning bath, the resultant silver particles are expected to be stable as in the original image but likely to be of increased stability.



Figure 7: Transmission electron micrograph of processed silver grains from Eastman Kodak Kodabromide Paper.



Figure 8: Transmission electron micrograph of silver grains from previous print after treatment in experimental restoration sequence.

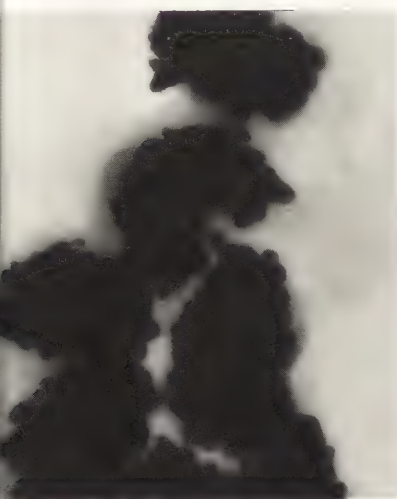


Figure 9: Transmission electron micrograph of silver grains from previous print after restoration treatment and subsequent toning in a Selenium bath.

1. Hendriks, K.B., B.L. Tom, C. Sergeant, C. Evans, J. Melnick, P. Poltras, and D. Nishimura. "Experiments on the Restoration of Discoloured Black-and-White Photographs in Chemical Solutions." In ICOM Committee for Conservation, 7th triennial meeting, Copenhagen, 10-14 September 1984, preprints, V.2: 84.14.34-84.14.37. Paris: International Council of Museums, 1984.
2. Von Ardenne, M. Zeitschrift für angewandte Photographie. 2:14; 1940.
3. Hall, C.E. and Schoen, A.L. "Application of the Electron Microscope to the Study of Photographic Phenomena" Journal of the Optical Society of America. 31(4):281-285; 1941 April.
4. Mees, C.E. Kenneth. "Recent Advances in the Theory of the Photographic Process" Journal of the Society of Motion Picture Engineers. 37:10-21; 1941 July.
5. Blake, R.K. and Meerkemper, B. "Developed Image Structure" Journal of Photographic Science. 9:14-25; 1955.
6. Koerber, W. "Über den Zusammenhang zwischen Morphologie und Farbe des entwickelten Silbers in photographischen Schichten" (On the Relationship Between Morphology and Colour of Developed Silver in Photographic Layers) In Wissenschaftliche Photographie: Ergebnisse der internationalen Konferenz für wissenschaftliche Photographie, ed. by Othmar Helwich, 535-538. Darmstadt: Verlag Dr. Othmar Helwich, 1958.
7. Weyde, E. "Grösse und Form des entwickelten Silberkornes und seine Beziehungen zu bildwichtigen Eigenschaften" (Size and Shape of the Developed Silver Grain and its Relationship to Image Properties) Photographische Korrespondenz. 98(1):7-12; 1962.



SUMMARY

The conservation problems in libraries and archives are not those of the individual objects but are in the masses of material to be kept and conserved. Because of the increasing masses of bad quality paper future conservation will become impossible.

One of the possibilities to decrease future conservation problems could be the introduction of standard specifications for permanent records and storage materials.

In the Netherlands these specifications are formulated and will be presented to the government.

One of the aims of this contribution is to stimulate the development of standard specifications not only for permanent records but also for file folders, mounting board, boxes etc.

THE DEVELOPMENT OF STANDARD SPECIFICATION FOR PERMANENT RECORDS IN THE NETHERLANDS

Judith H. Hofenk de Graaff
Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam
The Netherlands

Introduction

During the last 25 years the author was involved in research programs for the conservation of archival and library materials. Degradation phenomena were studied, conservation methods developed, deacidification problems investigated. Solutions were found for particular problems. For those problems, e.g. the conservation of an important charter, a complicated leather binding and even the conservation of some hundreds of printed papers solutions were found in agreement with the high standards of conservation nowadays required.

It became, however, more and more clear that the real conservation problems in archives and libraries are not those of the individual object but are in the masses of material to be kept and conserved.

How to handle the millions of 19th century books and newspapers, acid and brittle? Archive materials of the last hundred years, kilometers of storage, made of paper varying from relatively good to very bad?

Mass deacidification is a world wide discussed topic but only partial solutions are found. The DEZ (Diethyl Zinc) method did give hope for the future, but problems arose. The Methoxy Magnesium Methyl Carbonate is becoming used in various types of equipment (1). The impregnation with calcium hydroxide followed by freezing and freeze drying have proved successful (2).

But even when these solutions are developed to an almost ideal system it will be not "The answer" for all our archive material. Mass conservation treatments will also ask for skilled labour and well trained conservators and when the masses of archival materials and books will increase in quantity and bad quality as it happens these days the future conservation of all this material will become impossible.

One of the possibilities of decreasing the future needs for conservation could be the introduction of government standard specifications for the quality of paper for permanent records.

The objective of such standards is to establish criteria for permanence of paper, that should last for several hundreds of years when kept under proper storage conditions.

As storage is an important factor in the permanence of books and archives it would be useful to equally develop standards for storage materials as filefolders, boxes etc.

One of the aims of this contribution is to stimulate the development of standard specifications for permanent records.

Basic principles for standard specifications

Although the literature on ageing of paper is extensive and well known (3,4) a short survey was made to characterize the typical ageing phenomena and the measures against it (5).

From the literature it becomes clear that:

- permanence is at least an approximate function of the pH of an aqueous extraction of the paper. Acid hydrolyzes of paper is one of the main causes of deterioration of paper. Consequently the remedy against it is the buffering with an alkaline filler.
- the acidity and consequently deterioration of 19th century paper is largely caused by the use of alum/rosin sizing. Consequently this type of sizing should be avoided in permanent paper.
- the quality of the pulp defines at least partially the quality of the paper produced. The presence of groundwood will cause accelerated yellowing and fragility of paper on ageing.

The specifications -based on the above mentioned ageing phenomena- should consist of the following elements:

- pH: the aqueous extract of paper should be at least neutral (pH7) but preferably in the alkaline region (pH7-10).
- buffercapacity: paper should contain a reserve buffering capacity that can neutralize acidic gases from the atmosphere (air pollution)

- composition: paper should be free of groundwood or unbleached woodpulp and made of good quality cotton or linenpulp or bleached woodpulp.
- sizing: paper should be neutrally sized; the use of alum/rosin sizing must be avoided.
- permanence: the ability of paper to resist the effects of natural ageing should be expressed by a percentage retention after artificial ageing.

Search for existing standard specifications

Having formulated the basic principles for standard specifications the search after existing ones begins.

The first and most important to come across are those from the American Society for Testing and Materials (ASTM) (6): D 3208-81, Manifold papers for permanent records, D 3290-81, Bond and ledger papers for permanent records, D 3458-75, Copies from office copying machines for permanent records; D 3301-74(1979) File folders for storage of permanent records.

Almost all these specifications contain the basic principles mentioned above.

Although the standard specifications are used as a model in other countries the standards are only a recommendation and not imperative.

This is proved by a recent standard of the American National Standard Institute (ANSI) (7) for permanence of paper for printed library materials where it is explicitly stated that "the use of American National Standards is completely voluntary".

A recent exception is the introduction of standards for permanent records media and storage in the State of Arizona (August 1985) based on ASTM D 3209-81, a.o. (8).

Through an extensive correspondence with colleagues in other countries it became clear that almost nowhere an imperative use of standard specifications does exist. Even the existence of particular specifications could only be traced in a few countries.

A few exceptions are worth mentioning here: in Italy a standard specification for museumboard does exist, which contains all the principle items listed above. From 1983 on all museumboard have to fulfil standard specifications formulated by the government (9).

In the F.R.G. the Bundesanstalt für Material Prüfung (BAM) have formulated a test program and some specifications for permanent documents and copies of these (10). The specifications are more or less based on the ASTM Standard D 3458-75.

The only, as far as my information ranges, well organized and by the government controlled series of standard specifications not only for paper, but also for writing materials, copying apparatus etc. are those of Sweden and Finland, who handle the same standards. In Scandinavia a project is financed by the NORDINFO-organisation and three research laboratories in Finland, Sweden and Denmark are involved. In this research project test methods and specifications for permanent records are going to be standardized in Scandinavian countries during 1987. (11).

Specifications of Standards in the Netherlands

In the Netherlands no standards for Permanent records do exist at this very moment. In 1922 existed a so called "Papierbesluit" which did regulate the papertrade and gave some specifications for testing materials. The "Papierbesluit" was withdrawn in 1977. This type of regulations can be authorized by a so called "Koninklijk Besluit" (Royal Decree) and then take effect for government purposes.

Based on the literature survey and the existing ASTM standards and Scandinavian standards the working group "Permanent Records" (12) decided to formulate standards for the Netherlands on this data. However, before formulating the standards some problems had to be solved.

The main testing methods to characterize and measure the strength of paper are the folding endurance and the tear strength. The longevity as a function of the retention after ageing is also tested by measuring the folding endurance. Besides the fact that the folding endurance is most under discussion because the coefficient of variation is very large and the test is very sensitive to changes in humidity. There are several methods available. The best known are the MIT Tester, ASTM D 2176 and the Schopper Tester, ASTM. D 643(5). The former is used in the

American standard specifications the latter in the Swedish/Finnish standards.

The problem is that the results of the two methods are incomparable and even on the retention after artificial ageing it is said that the two methods are incomparable.

To test this phenomenon a serie of ten papers has been tested with the two methods before and after ageing. The results concerning the folding endurance are incomparable indeed, but the percentages of retention after ageing are similar (13).

As in Europe the Schopper Tester is used most it seems appropriate to use this method in the standards for the Netherlands.

Another difficulty, which is still not solved, is the use of artificial ageing to define the stability of paper to maintain initial properties over a long period of time.

There is a world wide discussion on the type of artificial ageing (14). The oldest method, based on Barrow's research, is the ASTM D 776, Relative Stability of paper (effect of heat on folding endurance). This method covers the heating of paper in an oven at 105°C during 3x24 h.

This method was written before extensive data were available on the effect of moisture on the ageing of paper.

It is now known that an accelerated ageing atmosphere should contain some moisture. The amount of moisture is a matter of opinion (15). A Tappi method requires ageing conditions of 90°C and 25% relative humidity and a draft International standard is in preparation (16).

Another ISO procedure is developed in F.R. Germany and suggest an ageing atmosphere at 80°C and 65% relative humidity (10).

As the discussions are not finished and the ASTM standard is, at this moment, the only official standard it was choosen for the standard specification in the Netherlands until another standard is authorized.

Considering the above mentioned data, the following specifications for permanent records have been formulated:

Composition and chemical requirements

- paper must be made from cotton or linen pulp, fully bleached woodpulp or a mixture of both. The paper must be absolute free of unbleached woodpulp or groundwood.
Recommended test methods TAPPI T 401-OM82 or ASTM D 1030
- Hydrogen Ion Concentration (pH). The paper extract must have a pH from 7,5 - 9,5 measured by the cold extraction method.
Recommended test methods: TAPPI T 509, NEN 2151
- Buffering capacity. The paper must contain an alkaline filler of calcium or magnesium carbonate. The minimum shall be 2% based on the oven dry weight of the paper, calculated as calcium carbonate.
Recommended test methods, ASTM D 3458/13,4
- The paper must be neutral sized and not contain alum or alum/rosin sizing.
Recommended test methods, TAPPI T 255, ASTM 3458.

Physical Requirements

Although no specific requirements are formulated on the weight per unit area, starting point is a weight of 80 g/m². When specific specifications are agreed between purchaser and seller the average deviation of each delivery may not be more than 5%.

- Brightness. The paper has a directional reflectance Elrepho R 457, measured with Xenonlight of at least 75%.
Recommended test methods, TAPPI T 452, NEN 1843.
- Internal Tearing Resistance. The average internal tearing resistance in each direction shall be not less then 60 g.
Recommended test methods TAPPI T 414, ISO 1974.
- Folding endurance. The minimum folding endurance, average of both directions shall be not less then 150 (Schopper Tester)
Recommended test methods: TAPPI T 423: ISO/DIS 5626.

Permanence

After accelerated ageing, the retention of internal tearing strength and folding endurance must be at least 80%.

The accelerated ageing must be carried out after ASTM 776 (3x24h. at 105°C) until another standard is authorized.

The working group "Permanent Records" in the Netherlands, shall -after having formulated the standard specifications- present these to the Dutch Government and ask for authorization by means of a "Koninklijk Besluit" so that all paper used by the government shall fulfil the above mentioned requirements.

The development of standard specifications for storage materials

During the research on the formulation of standard specifications for permanent records much knowledge was obtained about paperquality and their permanence. The logical consequence of working on standards for new paper was the consideration about future storage of these papers in archives.

Beside carrying out conservation research one of the functions of the Central Research Laboratory for Objects of Art and Science in the Netherlands is to assemble knowledge and to transfer this knowledge into the conservation field. One of the tools for this transfer is the organization of working groups.

In the working group "Archival Conservation" state, provincial, and municipal archives as well as conservators and conservation scientists are represented.

In this group the need for standard specifications for storage materials was urgently expressed. Based on the above described research it was quite easy to formulate standards for file folders.

The following standard was developed:

Standard specifications for file folders for storage

Composition and chemical requirements

- Paper must be free of unbleached woodpulp or groundwood ($< 0,1\%$)
- The pH of the cold extraction of the paper must be from 7,5-9,5
- The paper must contain an alkaline filler of calcium or magnesiumcarbonate. The minimum shall be 2% based on the weight of the paper, calculated as calciumcarbonate.
- The paper must be neutrally sized and not contain alum or alum/rosin sizing.

Physical requirements

Although no specific requirements are formulated on the weight per unit area, in consultation with the state archives paper with a weight of 135 g/m^2 is chosen.

- paper shall be white or have a light colour. If coloured this should be water resistant. Measured by means of a standard Grey Scale 4-5. Testmethod ISO R 105.
- Paper shall have an average internal tearing resistance of minimum of 130 g. Testmethod TAPPI T 414.
- The minimum folding endurance, average of both directions, shall be not less than 300 (Schopper tester) TAPPI 423 OM-84

Permanence

After accelerated ageing the retention of the internal tearing resistance and folding endurance must be at least 80%.

This standard is now accepted by the State Archives and material is produced after the specifications.

The file folder is especially produced for the State Archives but can be obtained in limited quantities by small archives and museums.

As the introduction of the standards for file folders was very successful the working group "Archival Conservation" has now started a project to characterize standards for storage boxes.

Acknowledgements

The author is indebted to Drs. Arnold J.M. den Teuling, Provincial Inspector for the archives in Drenthe, on whose initiative the project started and for his enduring stimulation.

The author is grateful to the two working groups "CCASA-project-groep kwaliteitseisen Permanent houdbaar papier" and "CL-Archief-restauratie" for their cooperation and patience during the project.

The author wishes to thank all those colleagues who have reacted on several questions through correspondence, in particular Dr. William K. Wilson, National Archives, Washington DC.

NOTES

1. G.M. Cunha, Mass deacidification systems available to librarians, *New Directions in Paperconservation*, Oxford, 14 - 18 April 1986.
2. O. Wächter, Lecture held on 13 Oct. 1986 for the Association of Archivists, Den Haag, The Netherlands.
3. J. Byrne, J. Weiner, *Permanence*, Bibliographic series no. 213, 1964, Supplement I, 1970, The Institute of Paper chemistry, Appleton.
4. W.K. Wilson, E.J. Sparks, Historical survey of Research at the National Bureau of Standards on materials for archival records, *Restaurator* 5, 1983, 191 - 241.
5. W.K. Wilson, E.J. Sparks, An analysis of the ageing of paper, *Restaurator* 3, 1979, 37 - 61.
6. ASTM, 1981 Annual Book of ASTM Standards, Part 20, Paper; Packaging; Business Copy Products, Philadelphia, 1975.
7. ANSI, *Permanence of Paper for Printed library materials*, ANSI Z 39.48-1984, New York.
8. State of Arizona, *State Records management Manual*, Record Management Records, Phoenix, 1984.
9. *Gazetta Ufficiale Della Repubblica Italiana*, n. 257, p. 7593, 19-9-1983, Normativa in materia di catoni destinati al restauro ed alla conservazione del materiale soggetto a tutela.
10. BAM, *Herstellung von Urschriften notarieller Urkunden gemäss 26 Abs. 3 Satz 2 an Dienstordnung für Notare und Herstellung von Ausfertigungen und beglaubigten Abschriften*. BAM, Berlin.
11. Information received through correspondence with Jouko Virtanen from the Technical Research Centre of Finland, Division of Information Technology, Graphic Arts Laboratory, Tekniikantie 3 SF - 02150, Espoo. The other laboratories are Statens Provningsanstalt Sweden, Mrs. Marie Louise Samuelsson and Dantest in Denmark, Mr. Age Skoo. The standard used in Finland is SFS 4465:S
12. In 1985 after some preliminary studies a workinggroup was installed, in which the ministry of Culture (WVC) and the ministry of Inner Affairs (BiZa) participated. A representative of the Dutch Cities (Vereniging van Nederlandse Gemeenten) was also member of the group. The technical members were an archivist, a conservator and a conservation scientist.
13. Report Vezelinstituut TNO, 1986.
14. W.K. Wilson, E.J. Parks, Comparison of accelerated Ageing of Book Papers in 1937 with 36 years Natural Ageing, *Restaurator* 4, 1980, 1 - 55.
15. R.W. Lanting, ed. *Veroudering en aantasting van cellulose door luchtverontreiniging, literatuur overzicht* TNO, Delft, 1985, hoofdstuk 7.
16. ISO, *Paper and Board, Accelerated Ageing, Part 2, Moist/heat treatment (low relative humidity)*, Draft International Standard ISO/DIS 5630/2, 1984.



RESUME :

Le renforcement à l'iodure mercurique des clichés gélatino-argentiques produit des images stables qui prennent une couleur jaune-citron plus ou moins uniforme accompagnée d'une perte de contraste. Après avoir mis en évidence la présence de sels de mercure et d'iodure d'argent dans des négatifs anciens détériorés, les auteurs se sont attachés à reproduire ces altérations par des vieillissements accélérés sur des négatifs souples modernes et sur des négatifs sur plaque de verre. Une méthode de restauration par développement a permis de restituer les contrastes et de stabiliser l'image. Le risque de décollement de la couche image de son support en verre lors de la restauration a été minimisé par le contrôle du pH du bain de re-développement.

LES NEGATIFS ALTERES PAR UN TRAITEMENT A L'IODURE MERCURIQUE : ANALYSE ET RESTAURATION

Bertrand LAVEDRINE, Françoise FLIEDER

Centre de Recherches sur la Conservation des Documents Graphiques
36 rue Geoffroy-Saint-Hilaire, 75005 Paris, France

Les négatifs gélatino-argentiques sur plaque de verre et support souple (nitrate et acétate de cellulose) présentent diverses dégradations qui sont aujourd'hui bien répertoriées (2). Parmi celles-ci, il en est une, spectaculaire, qui se traduit par un jaunissement de l'image, différent de celui produit par le thiosulfate résiduel ; il en résulte une perte de densité et une atténuation des contrastes. Afin de mieux comprendre les causes et les mécanismes de cette coloration, il est nécessaire d'analyser des clichés anciens et de reproduire cette altération sur des négatifs modernes. L'objet de cette communication est de présenter les résultats de l'étude que nous avons faite dans ce sens ainsi que la méthode mise au point pour restaurer les images altérées.

Analyse au microscope électronique à balayage d'un négatif altéré

L'analyse au microscope électronique à balayage équipé d'une microsonde nous a révélé, sur un fragment de plaque altérée, la présence d'argent, d'iode et de mercure (figure 1). Nous avons donc sélectionné dans la littérature les traitements où ces composés interviennent, en particulier le renforcement à l'iodure mercurique. Cette technique semble avoir été très répandue au début du siècle. En effet, les conditions aléatoires de prise de vue ont conduit les photographes à pratiquer postérieurement des corrections pour ajuster la densité des négatifs. En cas de sous-exposition, le renforcement à l'iodure mercurique permet une intensification progressive du négatif.

Préparation d'échantillons traités à l'iodure mercurique

Afin de reproduire ce type d'altération, nous avons soumis des négatifs modernes (gamme de gris) à ces traitements de renforcement. Deux formules ont été expérimentées : la première (dite de KIRCHOFF) (6) est une solution de chlorure mercurique, d'iodure de potassium et de thiosulfate de sodium. La seconde, préconisée par MM. LUMIERE (7), est une solution d'iodure mercurique et de sulfite de sodium.

Sur les échantillons ainsi traités, on a observé un gain uniforme de densité (figure 2) et une coloration vert foncé de l'image.

Ces négatifs ont été ensuite placés dans des enceintes climatiques à une température de 70°C à des humidités relatives différentes (50 % H.R. et 90 % H.R.).

Pour les deux formules de renforcement, la couleur des échantillons évolue avec le temps de façon similaire du vert foncé au jaune clair.

De même, la densité diminue progressivement (figure 3). Quel que soit le traitement, l'humidité accélère considérablement ce phénomène (figure 4).

Analyse des échantillons en diffraction X et étude des mécanismes de dégradation

- Analyse (cf. tableau)

La spectrométrie de diffraction X nous a permis d'identifier certains composés minéraux cristallisés présents dans les échantillons renforcés à l'iodure mercurique, avant et après vieillissement (figures 6 et 8).

Dans les deux cas, nous avons relevé la présence d'iodure d'argent. L'iodure mercurique, mis en évidence lors des mesures effectuées avant vieillissement (figure 6), semble disparaître au cours de celui-ci (figure 7). Après 15 jours de vieillissement accéléré à 70°C, 90 % H.R., il n'en subsiste que des traces (figure 8).

Les mesures faites sur des négatifs anciens dégradés montrent des résultats proches de ceux obtenus sur des échantillons vieillis artificiellement (figure 9).

- Etude des mécanismes de dégradation

Lorsqu'on plonge le négatif dans un bain de renforcement, l'argent qui compose l'image se transforme partiellement en iodure d'argent jaune et en un mélange iodure mercurique-mercure de couleur vert foncé (1). Ces composés augmentent notablement la densité de l'image. Cependant, l'iodure mercurique n'est pas stable : à la chaleur et à la lumière, il se décompose en mercure et iodure mercurique qui peut à nouveau réagir avec l'argent (9). Au cours du vieillissement, il est probable que ce cycle se renouvelle jusqu'à la transformation de tout l'argent en iodure. L'image finale sera donc composée uniquement d'iodure d'argent de couleur jaune et de mercure.

Il y a sans doute des réactions plus complexes qui rentrent en jeu dans ce processus*. On peut néanmoins schématiser les réactions :

* L'iodure mercurique seul ou mélangé à l'iodure d'argent a fait l'objet d'étude pour réaliser des émulsions à noircissement direct et à développement (8).

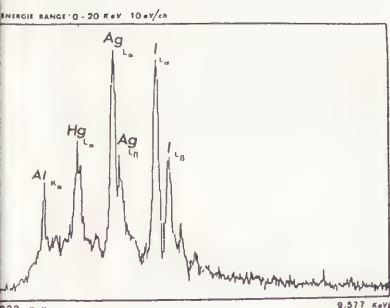
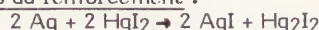
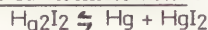


figure 1 : analyse d'un échantillon de négatif dégradé sur plaque de verre
MEB : Jeol JSM-35 C
Microsonde ORTEC system 5000

- au cours du renforcement :



- au cours du vieillissement :



Restauration

L'altération de l'image étant le résultat de la transformation de l'argent en iodure d'argent, il suffit de développer à nouveau l'image pour inverser le processus et réduire l'iodure d'argent en argent métallique.

Plusieurs révélateurs sont proposés dans la littérature comme le Rodinal (Agfa) (4) ou le Dektol (Kodak) (5). Nous avons expérimenté ce dernier (dilué 1:1) sur des films modernes et sur des négatifs sur plaque de verre, renforcés et vieillis artificiellement.

Afin d'améliorer l'action du révélateur, il s'est avéré indispensable d'exposer les phototypes plusieurs minutes à une forte source lumineuse (lumière solaire, lampe xénon).

De bons résultats ont été obtenus sur les films modernes. La courbe caractéristique est à peu près restituée sauf dans les hautes densités (figure 10). Le film reprend sa tonalité gris-neutre. Pour les plaques anciennes, les résultats sont moins concluants. Le cliché est intensifié par passage dans le révélateur. Malheureusement, dans la majorité des cas, la gélatine gonfle, se fragilise et a tendance à se détacher du support lors du lavage. La brusque variation du pH entre le révélateur (pH = 11) et l'eau de rinçage (pH = 6,5) semble être la cause principale de cette altération. Nous nous sommes donc attachés à trouver un révélateur actif dont le pH soit près de la neutralité. Les formules, proposées par HAIST (3) à l'éthylène-diamine-tétracétique, sont particulièrement adaptées au développement des émulsions à l'iodure d'argent. De plus, elles peuvent être utilisées dans une large gamme de pH. Deux révélateurs de cette famille ont été testés, l'un aux sels de fer, l'autre aux sels de titane.

Le révélateur à l'ion complexe fer-ferreux éthylène-diamine-tétracétique ne donne pas de résultat satisfaisant en milieu légèrement acide. L'image se développe irrégulièrement et malgré un traitement prolongé, des traces jaunes subsistent sur l'émulsion.

Le révélateur à l'ion complexe titaneux-éthylène-diamine-tétracétique est plus actif sur les gammes de gris altérées de façon artificielle (figure 11). Malgré un léger voile de base (0.05), la courbe caractéristique a été à peu près restituée.

L'analyse par spectrométrie de diffraction X montre la disparition de l'iodure d'argent, transformé en argent métallique par le révélateur.

Nous avons appliqué ce traitement à quelques négatifs sur plaque de verre datant du début du siècle. L'image a été intensifiée, la coloration jaune a disparu et aucun décollement de la couche image n'est survenu lors du lavage.

Stabilité du phototype après la restauration

Afin de s'assurer de l'innocuité à long terme de ce traitement, les phototypes restaurés au révélateur TiEDTA ont été placés dans des enceintes climatiques. Les conditions thermohygrométriques étant assez drastiques (15 jours, 70°C, 90 % H.R.), nous avons ajouté un échantillon de référence qui n'a subi aucun traitement correcteur. Nous pouvons ainsi différencier la dégradation due aux conditions climatiques seules, de celles produites, éventuellement, par la restauration. Aucune altération n'a été décelable visuellement.

Mesure de la densité avec le filtre visuel :

On note une perte générale de densité d'environ 5 % (figure 13). Sur l'échantillon de référence, la variation est globalement la même.

Mesure de la densité avec le filtre bleu :

On observe une différence de comportement entre l'échantillon de référence et le négatif restauré. Ce dernier présente une perte de 8 % pour les densités maximales (D max.) et reste inchangé aux densités minimales (D min.) (figure 13). Sur le témoin, on observe au contraire un gain de densité pour les (D min.) et peu de variation aux D max. (figure 12).

Nous n'avons pu établir les raisons de ces comportements opposés, il peut s'agir de réactions entre des produits résiduels non cristallisés que nous n'avons pu mettre en évidence par la diffraction X. Il faut cependant noter que les courbes caractéristiques mesurées avec le filtre bleu et le filtre visuel du film témoin sont à peu près les mêmes. Les films restaurés présentent une absorption plus prononcée dans le bleu. Une diminution de cette absorption n'a que peu de conséquence pour un tirage noir et blanc. On peut donc considérer cette technique de restauration comme satisfaisante.

L'expérience a été répétée sur des films restaurés au Dektol, les résultats sont similaires (figure 14) avec néanmoins une altération plus prononcée.

Conclusion

Ce travail confirme le manque de stabilité des phototypes qui ont subi un renforcement à l'iodure mercurique. Les produits résiduels oxydent lentement l'argent pour former de l'iodure d'argent qui confère à l'image une tonalité jaune. Cette altération se stabilise lorsque tout l'argent a été transformé. L'utilisation pour la restauration de ces négatifs d'un révélateur aux ions titaneux éthylène-diamine-tétracétique s'est révélé une méthode efficace ne produisant aucune altération prononcée à long terme.

La possibilité de travailler avec un pH proche de la neutralité nous conduit à conseiller cette technique plutôt que celle déjà décrite utilisant un révélateur alcalin comme le Dektol. Il faut cependant se garder de généraliser l'usage de ces restaurations chimiques car souvent un simple contretypage permet de restituer les contrastes du phototype si l'altération est uniforme.

BIBLIOGRAPHIE

- (1) FRANCOIS (M.).- Sur la couleur de l'iodure mercurique amorphe.- In : **Journal de Pharmacie et de chimie**, 6, 6, 1897, pp. 529-533
- (2) GILLET (M.), GARNIER (C.), FLIEDER (F.).- Glass plate negative.- In : **Restaurator**, 7, 1986, pp. 49-80
- (3) HAIST et al.- In: **Photographic Engineering**, déc. 1956, pp. 182-189
Cf. : GLAFKIDES (P.).- Chimie et Physique photographiques.- 5e éd., Tome 1 .
Paris : Editions de l'Usine Nouvelle, 1987, p. 122
- (4) HANSCH (M.).- Frühe Photographien ihre Technik und Restaurierung.- Überherrn :: Kabinett-Verlag Uwe Scheid, 1985
- (5) JOHNSEN (J.S.).- The Treatment of discoloured glass plate and cellulose nitrate negatives.- In : **Preprints de la 10ème conférence anniversaire de l'Institut of Paper Conservation (I.P.C.)**, Oxford, Grande-Bretagne, 14-18 avril 1986, D 27-D 29
- (6) LONDE (A.).- Aide-mémoire de la photographie.- Paris : J.M. Baillière et fils, 1897
- (7) MATHET (L.).- Traité de chimie photographique;- Paris : Charles Mendel, 1901
- (8) VAN DER MEULEN (P.A.), GILMAN (P.B.).- Photo-sensitive composition. U.S. Patent n° 2-874-047, February 17, 1959
- (9) VARET (R.).- Recherches sur les sels de mercure.- In : **Annales de Chimie et de Physique**, septième série, 8, 1896, pp. 79-141

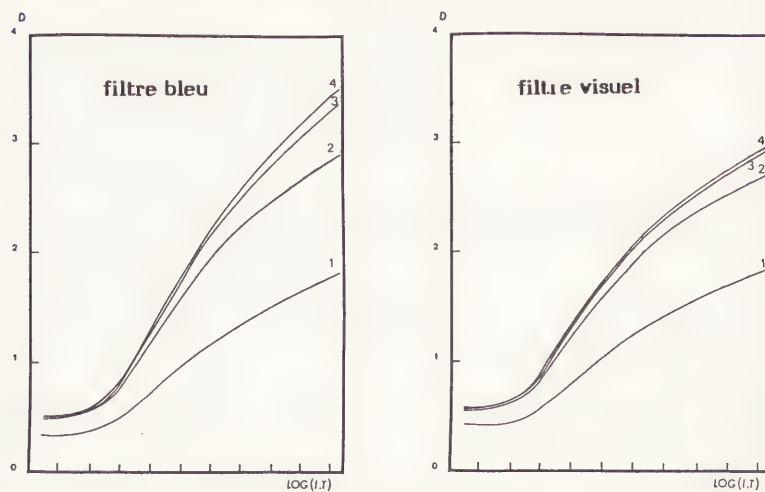


Figure 2 : renforcement de M. Lumière

1 - témoin

3 - bain de renforcement 5 mn à 20°C

2 - bain de renforcement 2 mn à 20°C

4 - bain de renforcement 8 mn à 20°C

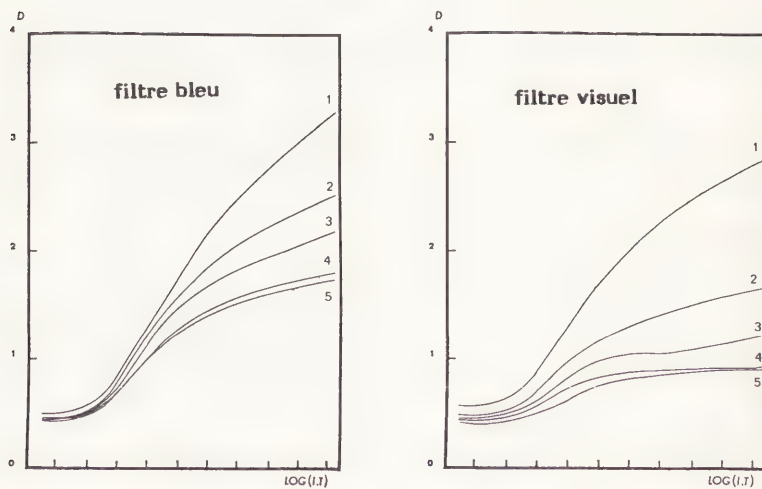


Figure 3 : vieillissement accéléré des échantillons renforcés 70°C, 90 % H.R.

1 - témoin

2 - après 16 h.

3 - après 46 h.

4 - après 65 h.

5 - après 141 h.

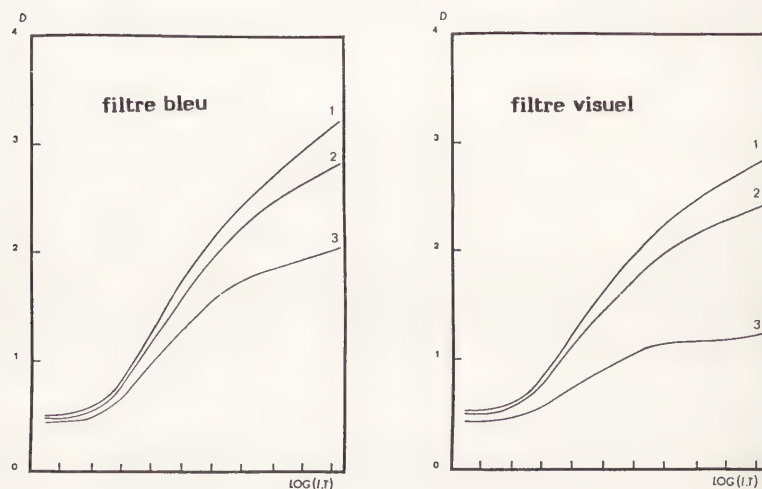


Figure 4 : influence de l'humidité lors du vieillissement des échantillons renforcés

1 - témoin

2 - après 3 j. 70°C, 50 % HR

3 - après 3 j. 70°C, 90 % HR

Tableau I
Analyse en diffraction X

AgI ASTM	Hg ₂ I ₂ ASTM	Spectre figure 5	Spectre figure 6	Spectre figure 7	Spectre figure 8	Spectre figure 9
$d(\text{\AA})$ I/I0	$d(\text{\AA})$ I/I0	$d(\text{\AA})$ I	$d(\text{\AA})$ I	$d(\text{\AA})$ I	$d(\text{\AA})$ I	$d(\text{\AA})$ I
	4,54 3		4,58 3a	4,54 4a	4,58	
3,98 6		3,98 6	3,98 4b	3,94 4b	3,96 4b	3,99 4
3,75 10		3,75 10	3,75 10b	3,73 10b	3,73 10b	3,78 10
3,51 4		3,51 2	3,51 4b	3,49 4b		3,54 3
	3,49 10		3,51 10a	3,49 10a		
	2,91 3		2,94 5a	2,95 4a	3,04	
2,73 2		2,73 1				
	2,47 3		2,45 3a	2,45 3a		
2,30 9		2,30 6	2,31 6b	2,28 8b	2,29 7b	2,30 4
	2,23 5		2,25 5a	2,23 3a		
2,12 3		2,12 2	2,11 3b	2,10 3b	2,11	2,13 1
1,96 5		1,96 4	1,96 4b	1,96 4b	1,95 3b	1,96 2

$d(\text{\AA})$: distance réticulaire

I : intensité estimée

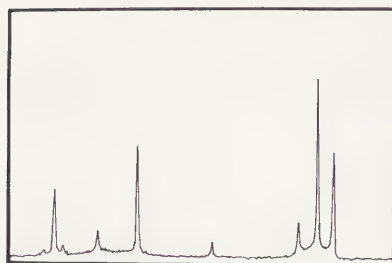


Figure 5 : AgI, Prolabo 21568 138

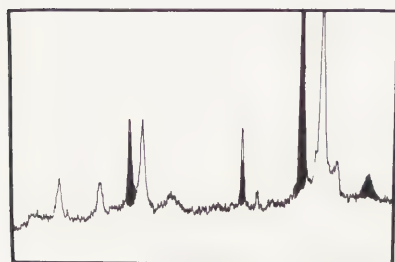


Figure 6 : négatif après renforcement
AgI, Hg₂I₂ pics sombres

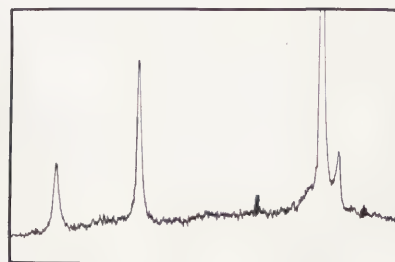


Figure 8 : négatif après vieillissement
AgI, Hg₂I₂ pics sombres

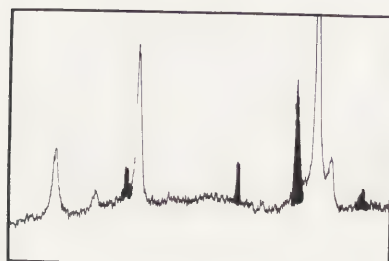


Figure 7 : négatif au cours du
vieillissement
AgI, Hg₂I₂ pics sombres

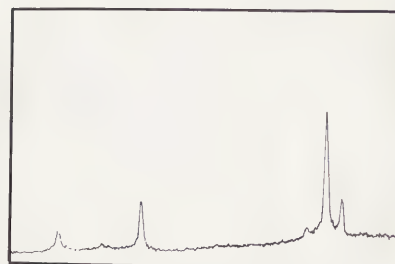


Figure 9 : négatif ancien altéré
AgI

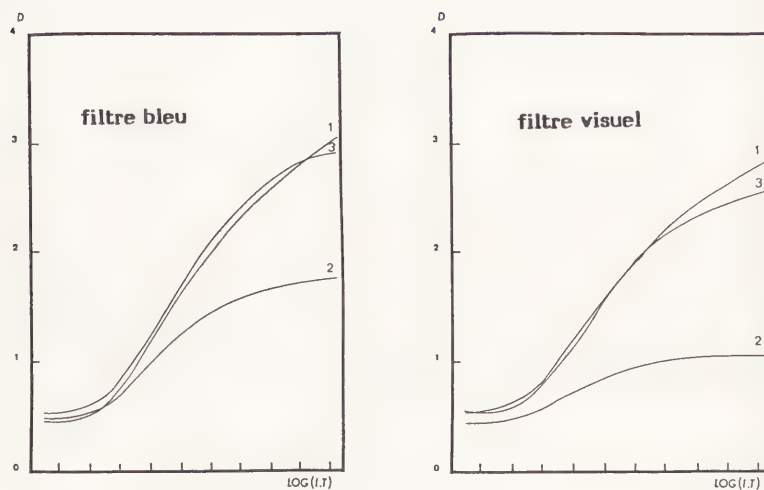


figure 10 : restauration au Dektol

1 - avant vieillissement accéléré 2 - après vieillissement accéléré
3 - après restauration au Dektol (dilué 1 : 1)

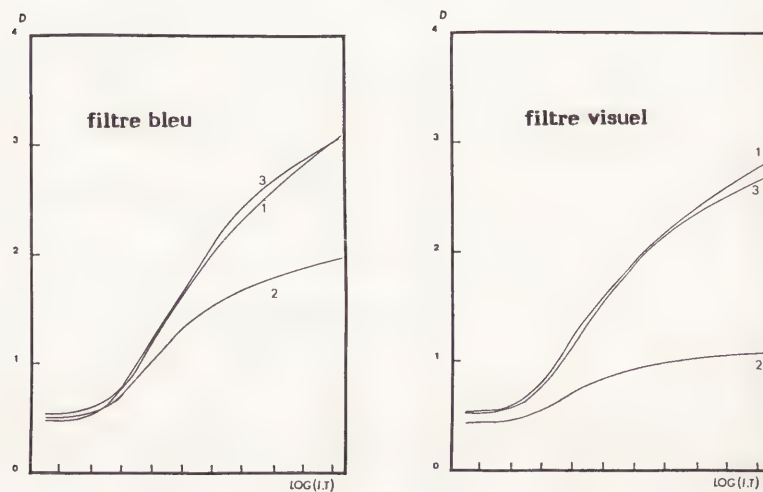
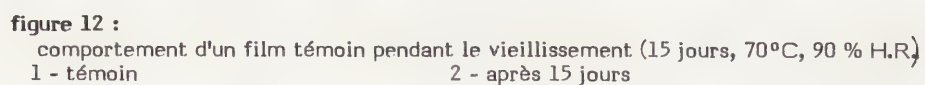


figure 11 : restauration Ti EDTA

1 - avant vieillissement accéléré 2 - après vieillissement accéléré
3 - après restauration Ti EDTA



Annexe

Mise en oeuvre expérimentale

Matériel

- négatif sur plaque de verre gélatino-argentique du début du siècle
 - gamme de gris de 21 plages réalisées avec du film GEVAPAN 36 (Négatif T 195)
 Les variations de densité ont été suivies avec un densitomètre MACBETH TR 924.
 Les enceintes climatiques marque HERAEUS VTKR 150 sont régulées à 90 % H.R. (+ %)
 et 70°C (+ 0,5°C)

- Traitement de renforcement

. Formule LUMIERE et SEYEWETZ :

{ eau	1000 ml
{ sulfite de sodium anhydre	100 g
{ iodure mercurique	10 g

. Formule KIRCHOFF :

{ eau	800 ml
{ bichlorure mercurique	10 g

Après dissolution, ajouter :

{ eau	100 ml
{ iodure de potassium	25 g

Il se forme un précipité rouge qui se dissout dans l'excès de réactif .

Ajouter alors

thiosulfate de sodium 1 g

Le cliché se renforce graduellement, il est ensuite lavé abondamment.

Restauration des négatifs jaunes

Les échantillons sont exposés plusieurs minutes à une source lumineuse intense (lampe xénon, lumière solaire), puis développés. Au cours du développement, ils sont exposés à différentes reprises à cette source lumineuse afin de suivre l'évolution du noircissement et de renforcer l'action du révélateur. Après environ 5 minutes à 24°C, le cliché acquiert une tonalité gris neutre uniforme. Il est alors lavé 10 minutes à l'eau distillée.

Les formules des révélateurs sont les suivantes :

. Révélateur Ti(EDTA)

{ solution à 20 % de chlorure titaneux	75 ml
{ Na ₄ EDTA	100 g
{ acétate de sodium	20 g
{ bromure de potassium	4 g
{ eau distillée pour faire	1000 ml

Lorsque nous avons préparé cette solution, son pH se situait aux alentours de 6,5. Cependant, il est possible de le modifier par addition d'acide chlorhydrique. Ce révélateur ne se conserve pas.

. Révélateur Fe (EDTA)

{ sulfate ferreux 7 H ₂ O	30 g
{ Na ₄ EDTA	100 g
{ bromure de potassium	0,5 g
{ eau distillée pour faire	1000 ml

Le pH est modifié par addition d'acide acétique ou de soude caustique.

. Révélateur Dektol

solution du commerce diluée (1:1)

RESUME :

Le but du présent travail était d'étudier l'influence de l'incorporation d'adhésifs à la pâte à papier destinée au colmatage des documents détériorés. Nous avons expérimenté trois produits : un amidon cationique, des fibres d'alcools polyvinyliques et une carboxyméthylcellulose. Différentes concentrations en adhésifs, employés seuls ou en mélanges, ont été essayées. Des papiers ont été greffés avec la pâte additionnée de ces colles, des vieillissements artificiels ont été réalisés pour les formules donnant les meilleurs résultats. L'étude a montré que les adhésifs amélioraient notablement la résistance des greffes. Notre choix a porté sur un amidon et des fibres d'alcools polyvinyliques.

LE COLMATAGE MECANIQUE DES DOCUMENTS : EFFET DE L'INCORPORATION D'UN ADHESIF DANS LA PATE A PAPIER

Françoise Leclerc, Françoise Flieder, Frédéric Bulle

Centre de Recherches sur la Conservation des Documents Graphiques
36 rue Geoffroy-Saint-Hilaire, 75005 Paris, France

Soumis à des agressions biologiques ou climatiques, le papier se fragilise. Les documents peuvent présenter des lacunes plus ou moins importantes qu'il faut combler pour leur redonner de la solidité. Le procédé traditionnel de réparation consiste à découper des empièchements de la taille des manques dans des papiers anciens ou des papiers japonais et à les faire adhérer, soit avec de la colle de pâte, soit avec des dérivés cellulotiques.

Peu à peu, on a tenté d'améliorer cette méthode de restauration en la mécanisant et en utilisant de la pâte à papier. Rappelons le principe de cette technique : de la pâte à papier, mise en suspension dans l'eau, est versée dans un récipient dont la base est constituée d'une grille qui supporte le document détérioré. Une succion est appliquée sous la grille, l'eau est éliminée et la pâte se dépose préférentiellement dans les lacunes.

Nous avons étudié au laboratoire la résistance de la greffe obtenue par la liaison entre les nouvelles fibres et celles du document à restaurer. A cette fin, des papiers ont été colmatés à l'atelier de restauration des Archives Nationales dans un appareil importé d'Israël, le Recurator.

Les premières expériences ont montré l'importance de certaines caractéristiques de la pâte employée. En effet, les fibres doivent être souples, assez courtes, fibrillées et avoir une bonne aptitude au gonflement dans l'eau pour bien s'accrocher aux fibres du document à restaurer. Si la pâte ne possède pas ces qualités, elles doivent lui être apportées par un raffinage réalisé dans une pile raffineuse. Le contrôle du raffinage est fait par la détermination de l'indice d'égouttage mesuré en degré Schöpper Riegler (°SR).

Nous avons précédemment défini que, pour une pâte de linters de coton déterminée, raffinée en pile Allimand aux Archives Nationales, le meilleur degré de raffinage était de 53°SR.

Le but du présent travail est d'étudier l'effet de l'incorporation d'adhésifs à la pâte sur la solidité des greffes.

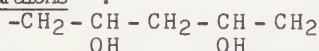
Choix des adhésifs

De nombreux auteurs conseillent d'introduire un adhésif dans la pâte destinée au colmatage.

NYUKSHA, ALKALAY et BAER (7-1-5) utilisent des émulsions d'acétate de polyvinyle (PVA) ou un mélange de PVA et de carboxyméthyl celluloses. Cependant, ces émulsions peuvent en vieillissant provoquer un jaunissement et d'autre part, elles sont généralement acides. NYUKSHA (8) emploie également des fibres d'alcool polyvinylique. BANSAL (3) incorpore à la matière fibreuse un mélange d'amidon cationique, de sel sodique de la carboxyméthylcellulose (NaCMC) à des concentrations allant de 1,8 à 7,2 %. BLUNN, PETHERBRIDGE et LORENZEN (5-6) préconisent d'ajouter à la pâte du NaCMC de l'amidon cationique ou des mannogalactanes à faible concentration. Notre choix a porté sur trois produits : un amidon cationique, le Solvitose N ; des fibres d'alcools polyvinyliques, les Kuralons ; une carboxyméthylcellulose, la Tylose C 300 p.

- Solvitose N* : c'est un éther d'amidon cationique prégélatinisé sur base de fécule de pomme de terre. Il se présente sous forme de paillettes blanches, sa solution a un pH de 9,5 à 20°C. Il est soluble à froid, on peut l'introduire sous forme solide, soit dans le pulpeur, soit dans la pile afin d'améliorer les caractéristiques mécaniques du papier. Quand il est ajouté sous forme de solution diluée dans la pâte, il améliore la rétention des charges et des particules de faibles dimensions.

- Kuralons** :



Nous avons sélectionné deux fibres d'alcools polyvinyliques, le Kuralon 105.2 et le Kuralon 103.

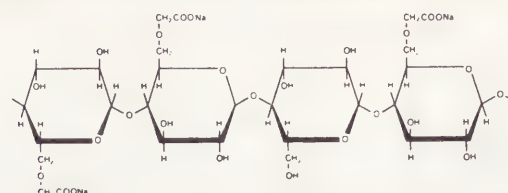
Le Kuralon 105.2 a un pouvoir d'adhésion important si lors de son séchage sous une presse chauffante à 60° les fibres ne sont que légèrement humides.

Le Kuralon 103 a une résistance à la traction plus forte que le précédent et même supérieure à celle des fibres naturelles. Sa température de fusion est voisine de 115°C, il se disperse facilement dans l'eau. Néanmoins, cette fibre est très floconneuse, d'où la nécessité d'une bonne homogénéisation de la solution.

* SOLVITOSE N : AVEBE 9607 PN Foxhol, Pays-Bas. Vendu en France par Paul Doittau, 91102 Corbeil Cedex, B.P. 103.

** KURALONS : KURARAI Co. Ltd, vendu en France par SEPPIC 60 rue Pierre Charron, 75008 Paris

- Tylose C 300 p* est une carboxyméthylcellulose sodique



Elle se présente sous forme de poudre blanche, faiblement jaunâtre soluble dans l'eau à n'importe quelle température. La solution aqueuse est neutre et possède, même à faible concentration, un pouvoir épaississant.

Fabrication du matériel d'essai et choix des tests

L'expérimentation a été menée d'une part sur des formettes, d'autre part sur des greffes.

Formettes

Ce sont des feuilles fabriquées en versant dans le bac du Recurator une quantité de suspension fibreuse nécessaire pour obtenir le grammage de papier désiré après égouttage de celle-ci sur la toile métallique.

Nous avons fait des formettes avec de la pâte de linters de coton raffinée à 53°SR additionnée ou non d'adhésifs.

Greffes

Elles ont été réalisées sur deux papiers différents : un vélin, 100 % pâte de linters de coton 160 g/m² et un papier édition, 100 % pâtes chimiques blanchies 80 g/m². Les feuilles sont déchirées en deux parties égales soit parallèlement au sens machine, soit perpendiculairement au sens travers du papier. Dans les deux cas, les deux morceaux sont positionnés sur le tamis du Recurator, avec un espace de 6 cm qui sera comblé par de la pâte.

Choix des tests

- Sur les greffes, nous avons effectué des essais de résistance mécanique : résistance à l'éclatement et à la traction**. La résistance à la traction est mesurée sur des éprouvettes découpées dans les papiers greffés, la force de traction est exercée perpendiculairement à la jonction. Les essais d'éclatement sont faits en centrant la greffe sur la membrane de l'éclatomètre. Nous avons également examiné au microscope électronique à balayage (MEB) l'état de surface des papiers greffés***.

- Sur les formettes, la blancheur et le pH**** ont été mesurés. Des vieillissements artificiels ont été réalisés à la chaleur humide (90°C et 60 % H.R. pendant 7 jours) sur les papiers greffés et sur les formettes contenant les adhésifs ayant donné les meilleurs résultats.

Choix de la concentration à employer pour les différents adhésifs

Nous avons travaillé uniquement sur du papier greffé.

Solvitose N :

Des concentrations de 0,5 à 1,3 % de produit par rapport à la pâte sèche nécessaire au colmatage ont été utilisées.

L'amidon a été introduit soit à l'état de poudre dans la pile, soit en solution dans la machine de colmatage ou dans les deux.

Les formules suivantes ont été essayées :

- 0,5 % et 1 % dans la pile
- 0,8 % et 1 % dans la machine
- 1 % dans la pile, 0,5 % dans la machine
- 0,5 % dans la pile, 0,8 % dans la machine
- 0,5 % dans la pile, 1 % dans la machine
- 0,5 % dans la pile, 1,2 % dans la machine
- 0,3 % dans la pile, 1 % dans la machine
- 0,7 % dans la pile, 1 % dans la machine

Les échantillons sont séchés entre des feutres sous pression de 2,5 bars pendant 24 heures.

Kuralons

Les fibres de Kuralons sont mises en suspension dans de l'eau à 20°C sous une faible agitation. Elles sont ensuite ajoutées à la pâte destinée au colmatage.

En nous rapportant à la littérature sur l'utilisation de ces fibres en papeterie, nous avons essayé :

- 4, 8, 12 % de Kuralon 105-2
- 4, 8, 12 % de Kuralon 103
- 4, 8, 12 % d'un mélange à 20 % de Kuralon 105.2 et 80 % de Kuralon 103
- 4 % d'un mélange 50/50 des deux produits
- 4 % d'un mélange à 80 % de Kuralon 105.2 et 20 % de Kuralon 103

* Tylose : HOESCHT, vendu par PROMO-INDUSTRIE, Z.I. des Chanoux, 101 Rode des Frères Lumière, B.P. 1, 93330 Neuilly-sur-Marne

** Normes AFNOR NFQ 03-053 et NFQ 03-004

*** Microscope Jeol J.S.M. 35 Cdu Laboratoire de Géologie du Museum National d'Histoire Naturelle (convention MNHN-CRCDG).

**** Norme AFNOR 03-038 et TAPPI T 435 m 51

Les papiers greffés sont placés sous une presse hydraulique à une pression d'environ 2,5 à 3 bars. Ceci permet à la greffe de garder une certaine humidité qui sera nécessaire au cours du séchage pour créer des liaisons entre les fibres d'alcools polyvinyliques et les fibres de coton. Le séchage se fait à une température de 60°C pendant 30 secondes sur chaque face du document. A cette température, seules les fibres de Kuralon 105 sont fondues.

Tylose

Nous avons expérimenté des concentrations en tylose de 1,2 et 4 %

La quantité nécessaire de tylose est additionnée à de l'eau à 20°C sous forte agitation pendant 30 minutes. Les papiers après colmatage sont séchés entre des feutres sous une pression de 2,5 bars pendant 24 h.

Interprétation des résultats (tableaux 1 à 6)

Les valeurs des résistances mécaniques sont assez dispersées avec des écarts-types souvent importants. Ceci peut s'expliquer par le manque d'homogénéité du matériau sur lequel ces tests sont effectués. Il s'agit en effet d'un matériau composite (papier-greffon).

Au cours de l'essai de traction, la rupture se fait toujours à l'endroit d'une des jonctions papier-greffon, par contre l'éclatement se produit parfois dans le papier ou dans la greffe. Ces dernières valeurs seront donc éliminées pour ne garder que celles correspondant à l'éclatement de la jonction.

Afin d'interpréter ces résultats, nous avons tracé autour de chaque point une zone d'incertitude définie par la valeur de l'écart-type attaché à chaque mesure. Le centre du graphique représente la valeur du témoin sans adhésif.

Dans l'ensemble, les dispersions sont plus importantes sur le papier édition que sur le papier vélin. Les variations des résistances à la traction sont plus significatives que celles de la résistance à l'éclatement.

Pour le Solvitose, les meilleures résistances ont été obtenues avec une concentration de 1 % ajoutée à la pâte dans la machine de colmatage.

En ce qui concerne les Kuralons, c'est le mélange à 4 % (par rapport à la pâte) des Kuralons 105.2 (80 %) et 103 (20 %) qui a été retenu.

La Tylose a donné de bons résultats à la concentration de 1 %.

Comparaison de l'effet des différents adhésifs sur les caractéristiques des papiers colmatés

Nous avons comparé l'effet des différents adhésifs aux concentrations retenues en les utilisant seuls ou en mélanges. Des greffes et des formettes ont ainsi été fabriquées avec les formules suivantes :

- 1 - 1 % Solvitose
- 2 - 4 % Kuralons : 80 % 105.2, 20 % 103
- 3 - 1 % Tylose
- 4 - 1 % Solvitose + 1 % Tylose
- 5 - 1 % Solvitose + 2 % Tylose
- 6 - 1 % Solvitose + 4 % Kuralons : 80 % 105.2, 20 % 103
- 7 - 1 % Tylose + 4 % Kuralons : 80 % 105.2, 20 % 103

Les caractéristiques mécaniques, la blancheur et le pH ont été mesurés avant et après vieillissement artificiel.

Résistance mécanique (graphiques 1 à 4) :

Comme précédemment, nous voyons que les résultats de la résistance à l'éclatement des greffes sont en général plus groupés que ceux de la résistance à la rupture. Les valeurs obtenues sur le papier édition sont dans tous les cas beaucoup plus dispersées. D'une façon générale, nous avons donné la préférence aux méthodes dont la résistance était la plus forte dans les deux sens et les résultats les plus homogènes.

Avant vieillissement, les meilleures formules sont les suivantes (citées par ordre préférentiel) :

- 4 % Kuralons : 80 % 105.2 et 20 % 103
- 1 % Solvitose + 4 % Kuralons : 80 % 105.2 et 20 % 103
- 1 % Solvitose + 2 % Tylose
- 1 % Solvitose

Après vieillissement, ce classement est légèrement différent :

- 4 % Kuralons : 80 % 105.2 et 20 % 103
- 1 % Solvitose
- 1 % Solvitose + 4 % Kuralons : 80 % 105.2 et 20 % 103
- 1 % Solvitose + 2 % Tylose

Observation au microscope électronique à balayage :

Nous voyons que les jonctions sont bonnes dans tous les cas. On n'aperçoit pratiquement pas la liaison entre le papier et la pâte. Sur la greffe effectuée avec les Kuralons, quelques fibres de PVA non fondues sont visibles sur la surface (photos 1 et 2).

Mesures de blancheur et de pH (tableau 7)

Dans l'ensemble, on peut considérer que les adhésifs n'ont pas provoqué de jaunissement, même après vieillissement artificiel, à l'exception peut-être du Solvitose qui semble avoir conféré à la formette une très légère coloration.

Les pH de tous les papiers encollés ne se sont pratiquement pas modifiés.

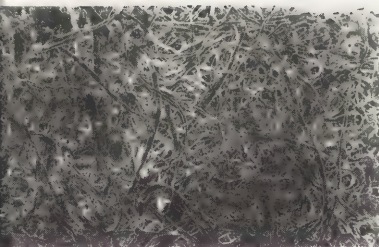


Photo 1 - Vue au MEB d'un papier édition greffé avec de la pâte additionnée de solvitose. Papier à gauche, greffon à droite. G = 60 X

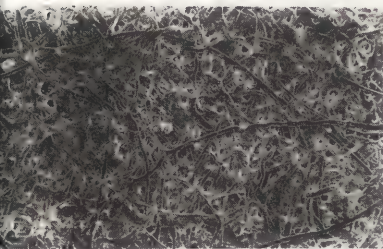


Photo 2 - Vue au MEB d'un papier vélin avec addition de Kuralons à la pâte. Papier à gauche, greffon à droite. G = 60 X

Conclusion

De ce travail, il ressort que l'adjonction d'adhésifs dans la pâte de linters de coton raffinée utilisée pour le colmatage améliore considérablement la résistance de la jonction papier-greffon.

Les fibres d'alcools polyvinyliques; un amidon cationique, et le mélange de ces deux produits, donnent d'excellents résultats. La carboxyméthylcellulose expérimentée est moins satisfaisante.

Bibliographie

- (1) ALKALAY (E.B.).- The History & development of Leaf-casting. In : **International Conference on the conservation of Library & Archive Materials & the Graphic Arts.**- Cambridge, London. Society of Archivists, Institute of Paper Conservation, 1980, pp. 187
- (2) BAER (N.).- An evaluation of P.V.A.C. adhesives. In : **Restaurator**, 2, 2, 1975, pp. 121-137
- (3) BANSÄ (H.).- Papieranfasern. Teil 2 : Anfasern, Verstärken und Trocknen. In : **Maltechnik Restauero**, 86, 1, janv. 1980, pp. 67-72
- (4) BLUNN (D.), PETHERBRIDGE (G.).- Leaf casting : the mechanical repair of paper artefacts. In : **The Paper Conservator**, 1, 1976, pp. 26-32
- (5) LORENZEN (N.).- Anfaserungsgerät STROMER I : technische Daten und Funktionsbeschreibung. Tiré à part, 1974, 6 p. 8 fig.
- (6) NYUKSHA (J.P.) & BLANK (M.G.).- Potchnaya liniya dlya Restavpatsiiknig. (Méthode de travail à la chaîne pour la restauration des livres).- Ed. Kniga, Moscou, 1976, 48 p. en russe
- (7) NYUKSHA (J.P.), BLANK (M.G.) & SALTYKOV-SHCHEDRIN (M.E.).- Restoration of paper with paper pulp containing polyvinyl alcohol fibres. In : **Congrès de ICOM, Comité pour la Conservation, 4e réunion triennale**, vol. 3, Rapport 15/13, Venise 1975
- (8) POURTALE (L.), LECLERC (F.), FLIEDER (F.), BULLE (F.), BARBIER (G.).- Le colmatage des papiers détériorés. In : **Les documents graphiques et photographiques. Analyse et Conservation**. Travaux du Centre de Recherches sur la Conservation des Documents Graphiques, 1984-1985.-Paris : Archives Nationales, 1986, pp. 11-52

Cette étude a été réalisée dans le cadre d'un programme de recherches financé par la Direction des Archives de France. Nous tenons à en remercier M. FAVIER, Directeur général des Archives de France.

Nous sommes également très reconnaissants de l'aide précieuse que nous ont apportée M. BARBIER et Mlle SAUCOIS, Chef et Sous-Chef de l'atelier de restauration des Archives Nationales, tout au long de ce travail.

Tableau 1

Effet de l'incorporation de solvite sur les résistances mécaniques
des greffes effectuées sur papier vélin

		Résistance à l'éclatement	Résistance à la traction	
		Indice	Longueur de rupture m.	Ecart-type
Pâte sans adhésif	SM ST	1,16 1,04	830 1070	29 50
Pâte + 0,5 % P	SM ST	1,10 1,10	920 1020	76 33
Pâte + 1 % P	SM ST	1,16 1,23	885 1275	72 80
Pâte + 0,8 % M	SM ST	1,28 1,23	1155 750	21 29
Pâte + 1 % M	SM ST	1,16 1,23	1225 1940	127 34
Pâte + 1 % P + 0,5 % M	SM ST	1,16 1,23	960 1430	29 76
Pâte + 0,5 % P + 0,8 % M	SM ST	1,13 1,16	795 1140	63 72
Pâte + 0,5 % P + 1 % M	SM ST	1,22 1,22	730 1085	0 63
Pâte + 0,5 % P + 1,2 % M	SM ST	1,16 1,23	735 1140	4 50
Pâte + 0,3 % P + 1 % M	SM ST	1,23 1,28	1015 1245	127 76
Pâte + 0,7 % P + 1 % M	SM ST	1,16 1,41	1020 1225	25 50

P = pile

M = machine

SM : sens machine
ST : sens travers

Tableau 2

Effet de l'incorporation de solvitose sur les résistances mécaniques
des greffes effectuées sur papier édition

		Résistance à l'éclatement	Résistance à la traction	
		Indice	Longueur de rupture m	Ecart-type
Pâte sans adhésif	SM	1,52	1095	68
	ST	1,42	1405	75
Pâte + 0,5 % P	SM	1,31	1360	105
	ST	1,42	1165	37
Pâte + 1 % P	SM	1,52	1320	166
	ST	1,31	1900	209
Pâte + 0,8 % M	SM	1,47	990	90
	ST	1,52	1660	271
Pâte + 1 % M	SM	1,52	1585	98
	ST	1,52	1750	226
Pâte + 1 % P + 0,5 % M	SM	1,42	1105	211
	ST	1,51	1595	166
Pâte + 0,5 % P + 0,8 % M	SM	1,31	1275	45
	ST	1,42	1140	98
Pâte + 0,5 % P + 1 % M	SM	1,31	1275	45
	ST	1,42	1140	98
Pâte + 0,5 % P + 1,2 % M	SM	1,31	1120	143
	ST	1,42	1020	75
Pâte + 0,3 % P + 1 % M	SM	1,96	1420	98
	ST	1,42	1465	128
Pâte + 0,7 % P + 1 % M	SM	1,52	1885	151
	ST	1,42	1215	120

P = pile

M = machine

SM : sens machine

ST : sens travers

Tableau 3

Effet de l'incorporation de Kuralons sur les résistances mécaniques
des greffes effectuées sur papier vélin

		Résistance à l'éclatement		Résistance à la traction	
		Indice	Ecart-type	Longueur de rupture m	Ecart-type
Pâte sans adhésif	SM	2,12	0,26	810	50
	ST	2,00	0,29	870	72
Pâte + 105.2, 4 %	SM	1,94	0,25	905	85
	ST	2,10	0,31	1030	97
Pâte + 105.2, 8 %	SM	1,84	0,14	685	67
	ST	2,04	0,11	830	29
Pâte + 105.2, 12 %	SM	2,56	0,14	1000	55
	ST	2,26	0,27	1240	110
Pâte + 103, 4 %	SM	2,34	0,17	695	135
	ST	2,13	0,22	825	140
Pâte + 103, 8 %	SM	2,24	0,18	605	38
	ST	2,36	0,16	720	21
Pâte + 103, 12 %	SM	2,32	0,20	815	0
	ST	2,26	0,23	825	46
Pâte + 4 % (20 % 105.2, 80 % 103)	SM	2,10	0,18	795	195
	ST	2,25	0,24	825	34
Pâte + 8 % (20 % 105.2, 80 % 103)	SM	2,37	0,17	790	68
	ST	2,29	0,18	900	55
Pâte + 12 % (20 % 105.2, 80 % 103)	SM	2,42	0,24	810	152
	ST	2,44	0,24	790	80
Pâte + 4 % (50 % 105.2, 50 % 103)	SM	2,44	0,22	680	38
	ST	2,49	0,16	925	63
Pâte + 4 % (80 % 105.2, 20 % 103)	SM	2,36	0,17	1020	29
	ST	2,42	0,14	1360	55

SM : sens machine
ST : sens travers

Tableau 4

Effet de l'incorporation de Kuralons sur les résistances mécaniques
des greffes effectuées sur papier édition

		Résistance à l'éclatement		Résistance à la traction	
		Indice	Ecart-type	Longueur de rupture m	Ecart-type
Pâte sans adhésif	SM	1,35	0,15	1125	37
	ST	1,53	0,26	1420	49
Pâte + 105.2, 4 %	SM	1,37	0,12	1480	60
	ST	1,42	0,17	1790	60
Pâte + 105.2, 8 %	SM	1,33	0,12	1280	105
	ST	1,33	0,15	1495	53
Pâte + 105.2, 12 %	SM	1,42	0,20	1130	218
	ST	1,32	0,10	1320	62
Pâte + 103, 4 %	SM	1,43	0,13	1265	62
	ST	1,33	0,14	1465	45
Pâte + 103, 8 %	SM	1,47	0,12	1265	106
	ST	1,34	0,10	1515	35
Pâte + 103, 12 %	SM	1,35	0,10	1465	98
	ST	1,58	0,16		
Pâte + 4 % (20 % 105.2 80 % 103)	SM	1,31	0,13	1170	135
	ST	1,29	0,13	1465	60
Pâte + 8 % (20 % 105.2 80 % 103)	SM	1,59	0,26	1335	45
	ST	1,51	0,19	1690	113
Pâte + 12 % (20 % 105.2 80 % 103)	SM	1,27	0,10	1200	113
	ST	1,56	0,16	1405	143
Pâte + 4 % (50 % 105.2 50 % 103)	SM	1,56	0,09	1550	37
	ST	1,64	0,17	1775	83
Pâte + 4 % (80 % 105.2, 20 % 103)	SM	1,62	0,10	1500	52
	ST	1,53	0,13	1650	45

SM : sens machine
ST : sens travers

Tableau 5

Effet de l'incorporation de tylose sur les résistances mécaniques
des greffes effectuées sur papier vélin

		Résistance à l'éclatement		Résistance à la traction	
		Indice	Ecart-type	Longueur de rupture m	Ecart-type
Pâte sans adhésif	SM	1,10	0,12	705	21
	ST	1,12	0,07	925	46
Pâte + 1 % tylose	SM	1,19	0,08	1045	72
	ST	1,17	0,05	1040	63
Pâte + 2 % tylose	SM	1,17	0,05	800	16
	ST	1,20	0,09	1000	131
Pâte + 4 % tylose	SM	1,07	0,12	910	29
	ST	1,01	0,04	960	59

SM : sens machine
ST : sens travers

Tableau 6

Effet de l'incorporation de tylose sur les résistances mécaniques
des greffes effectuées sur papier édition

		Résistance à l'éclatement		Résistance à la traction	
		Indice	Ecart-type	Longueur de rupture m	Ecart-type
Pâte sans adhésif	SM	1,25	0,14	925	75
	ST	1,33	0,22	1255	15
Pâte + 1 % tylose	SM	1,38	0,18	1200	67
	ST	1,55	0,06	1400	68
Pâte + 2 % tylose	SM	1,41	0,19	1480	151
	ST	1,74	0,11	1420	98
Pâte + 4 % tylose	SM	1,55	0,18	1465	75
	ST	1,55	0,06	1640	37

SM : sens machine
ST : sens travers

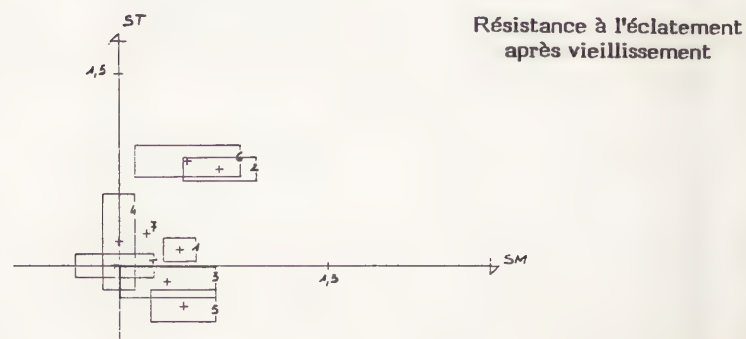
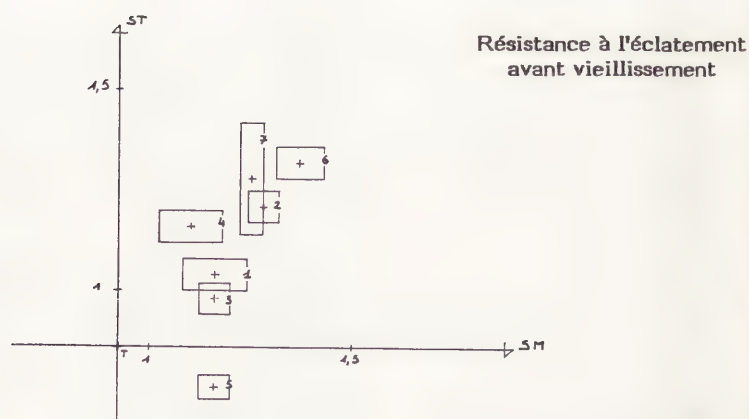
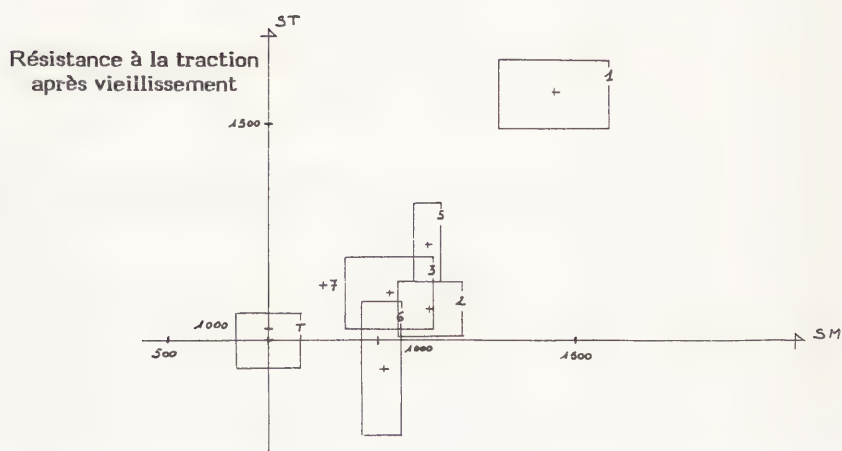
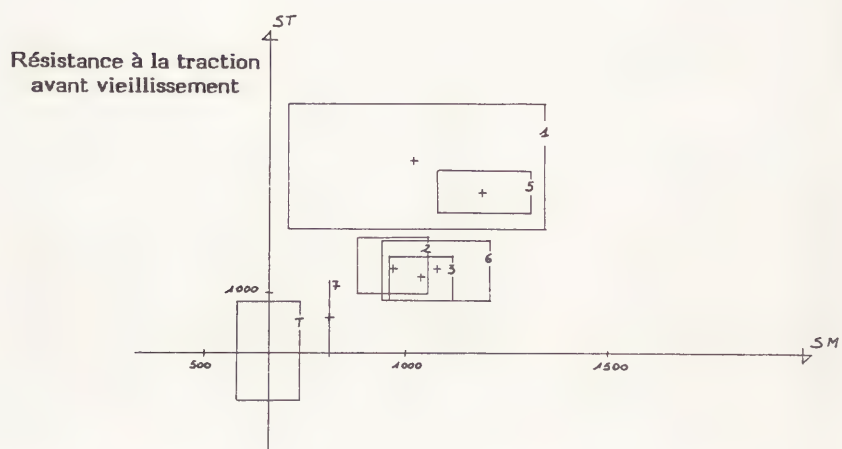
Tableau 7

Effet de l'incorporation d'adhésifs sur les blancheurs et les pH
de formettes avant et après vieillissement artificiel

	Blancheur				pH	
	Avant vieil.		Après vieil.		Avant vieil.	Après vieil.
		Ecart type		Ecart type		
Pâte sans adhésif	96,8	0,47	84,7	0,89	8,07	7,53
Pâte + 1 % solvitose	94,3	0,81	82,3	1,21	8,25	7,47
Pâte + 4 % Kuralons (80 % 105.2, 20 % 103)	97,0	0,58	82,3	1,21	8,25	7,64
Pâte + 1 % tylose	98,2	0,62	87,4	0,53	7,63	7,55
Pâte + 1 % solvitose + 1 % tylose	98,1	0,89	88,6	0,46	7,73	7,47
Pâte + 1 % solvitose + 4 % Kuralons (80 % 105.2, 20 % 103)	98,7	0,48	86,5	1,15	8,13	7,46
Pâte + 1 % tylose + 4 % Kuralons (80 % 105.2, 20 % 103)	97,7	0,65	86,9	0,65	8,15	7,63

Graphique 1

Résistances mécaniques des greffes sur papier vélin



T : témoin sans adhésif

1 - 1 % solvitose

2 - 4 % Kuralons
(80 % 105.2, 20 % 103)

3 - 1 % tylose

4 - 1 % solvitose
1 % tylose

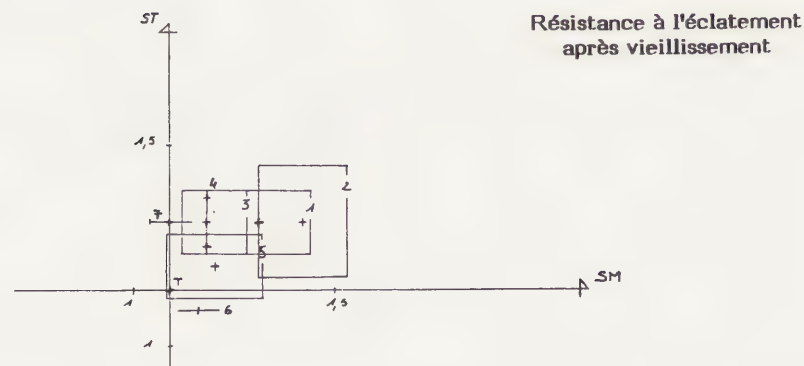
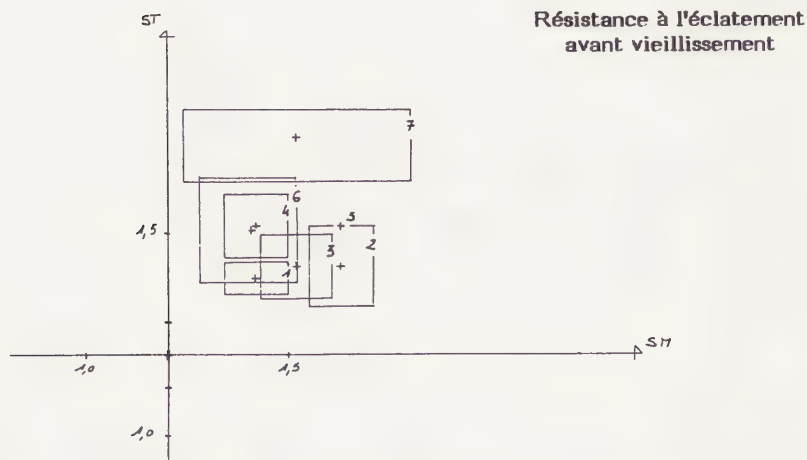
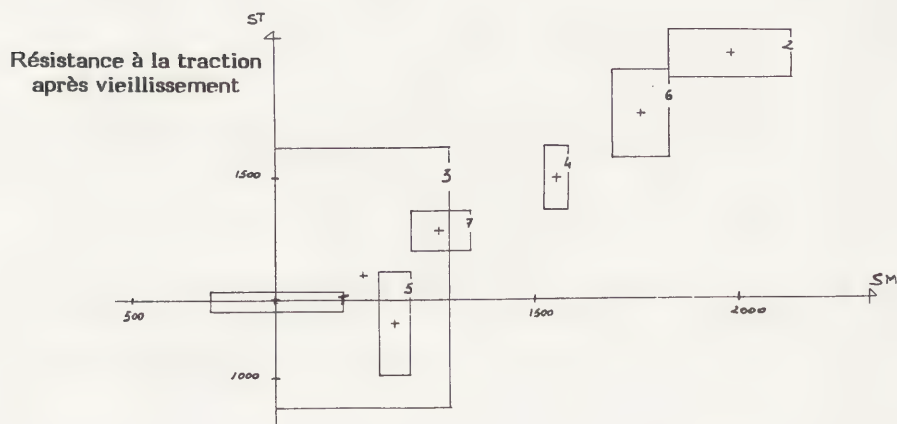
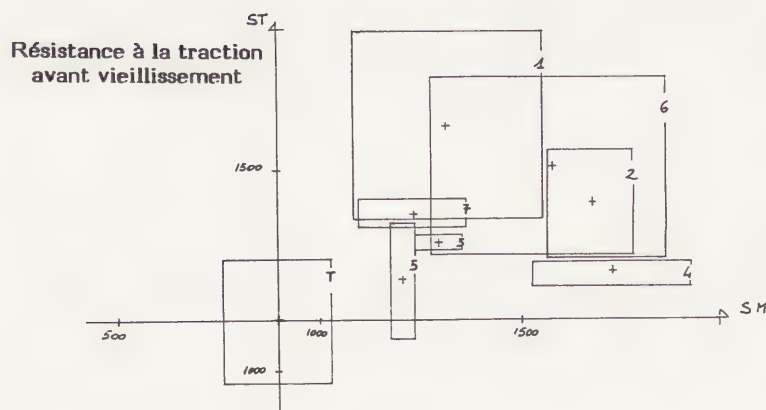
5 - 1 % solvitose
2 % tylose

6 - 1 % solvitose
4 % kuralons
(80 % 105.2, 20 % 103)

7 - 1 % tylose
4 % kuralons
(80 % 105.2, 20 % 103)

Graphique 2

Résistances mécaniques des greffes sur papier édition



T : témoin sans adhésif

1 - 1 % solvitose

2 - 4 % Kuralons
(80 % 105.2, 20 % 103)

3 - 1 % tylose

4 - 1 % solvitose
1 % tylose

5 - 1 % solvitose
2 % tylose

6 - 1 % solvitose
4 % kuralons
(80 % 105.2, 20 % 103)

7 - 1 % tylose
4 % kuralons
(80 % 105.2, 20 % 103)



SUMMARY

The problem is formulated to define the role of book paper lamination by a polyethylene film to prevent fungal deterioration. Four estimate techniques for the resistance to three species of fungi were taken, namely, determination of the gaseous products of destruction, infrared absorption spectra, alkali-soluble cellulose fraction in book paper and respiratory quotient of the fungi growing on samples. It is found that fungal growth is inhibited by paper lamination to some extent but this never provides biological resistance of documents in storage. Paper stabilisation with respect to the biological factor is necessary prior to lamination.

PAPER LAMINATION: BIOLOGICAL ASPECTS

Yu.P. Nyuksha, L.E. Sergeeva
M.E. Saltykov-Shchedrin State Public Library
18, Sadovaya
191059 Leningrad, USSR

Paper lamination has been used in the restoration practice for more than 50 years. Its techniques change with time. Various materials have been tested for paper lamination. In many restoration laboratories at present lamination is performed with a polyethylene film. Low-density polyethylene with a softening point of 110-120 °C is used for this purpose. The polyethylene film combines fairly well with document and significantly enhances its wear resistance. Many other properties of laminated documents have been studied. It is found that they are distinguished by their enhanced mechanical strength and durability. The question of their bioproofness remains to be a debatable one. In this connection it is important to note at least three considerations. First, the layer of polyethylene is not solid on the paper surface. It has a great many small holes of different form. Second, polyethylene films are capable of passing water vapours inside. The latter are adsorbed by the fibres and can hardly find their way to environment. Therefore, equilibrium moisture content of the film-covered paper is usually maintained at a higher level. Third, under the action of temperature and, especially, luminous radiation the polyethylene layer is subjected to ageing and there occurs a decrease in polyethylene crystalline state and an increase in the amorphous phase which is less resistant to exposure. All in these peculiarities of the paper enclosed in polyethylene contribute to fungal deterioration.

It has been known that many polyolefines including polyethylene are susceptible to fungal deterioration /4/. Fungi are especially active in the presence of polyethylene oxidation products /5/. Reduced biological resistance of laminated paper is therefore quite probable. Experiments on testing of fungi viability under different lamination conditions have led to the conclusion that lamination process is a questionable procedure to provide long-term storage.

The purpose of this work was to investigate specific features of fungal damaging of the polyethylene-laminated paper compared with original paper. Estimates were made using a test complex consisting of four factors, namely, taking account of the gaseous paper destruction products by gas chromatography permitting determination of minute quantities of the substances investigated /2/; definition of infrared absorption spectra of the affected samples, the method of IR-spectroscopy has proved to be a success /1/; taking account of the quantity of oxygen consumed by fungi, which permits a calculation of the respiratory quotient; definition of alkali-soluble fraction of the cellulose samples.

The following materials and methods were used: paper of experimental make manufactured from cotton fibres with a mass of 1 m² equal to 80 g and a polyethylene film, 15 μm thick. The paper was laminated at a temperature of 115 °C during 1 min. The samples having a size of 10x30 mm were prepared in two versions, namely, with cut and with soldered edges over the perimeter.

The tests were performed using fungi of the following species: *Aspergillus terreus* Thom, *Chaetomium globosum* Kunze:Fr., and *Trichoderma viride* Pers.:Fr.

Conidial suspension (titer, 10⁶ conidia/ml) to the amount of 0,1 ml was applied to each sample. The samples were placed on Czapek agar without a carbon source, with an interleaf of capron sieve. They were incubated in airtight bottles of 16 ml capacity. Carbon dioxide (CO₂) and oxygen (O₂) content inside the bottles was determined during regular observations of the colonial growth. A gas chromatograph with 2 m columns of 4 mm inner diameter was used for the measurements. Polysorb-1 was the adsorbent. Helium was used as the carrier gas. The following conditions were maintained during separation of the constituents: thermostat temperature, 50 °C; detector current, 150 mA; rate of the carrier gas, 60 cm³/h; transport speed of the chart strip, 60 mm/h. The constituents were eluted in the following order: 1.5 min retention time for O₂ and 2 min for CO₂ after introduction of the sample.

The constituents were identified by results of chromatography of the standard samples with assigned gas composition. Quantitative content of each constituent was found from the area of appropriate

peak on the chart strip. The alkali-soluble fraction was determined in a 1% NaOH solution using the well known technique.

Infrared absorption spectra were recorded by a UR-90 spectrophotometer in a range of 700-1900 cm^{-1} . Samples made of paper or of fungus biomass in the form of pressed tablets were prepared for recording the absorption spectra.

The experiments yielded the following results. Figures 1-3 show dynamics of the changes in the quantities of consumed oxygen and liberated carbon dioxide as well as values of the respiratory quotients. The amounts of CO_2 and O_2 change several hundreds of times during the experiment, therefore the curves were plotted by their decimal logarithms. The respiratory quotient is shown in the original numerical form because it changed within a small range only. All curves in question result from binomial approximation of the experimental points by the method of least squares.

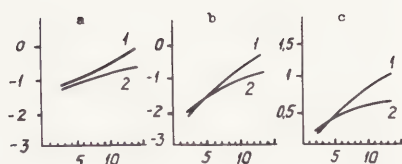


Fig. 1: Curves for gas exchange between *Aspergillus terreus* growing on control (1) and that on polyethylene-laminated paper. Abscissa - exposure, days. Ordinate: a - decimal logarithm of absorbed oxygen, mmol; b - decimal logarithm of liberated carbon dioxide, mmol; c - respiratory quotient.

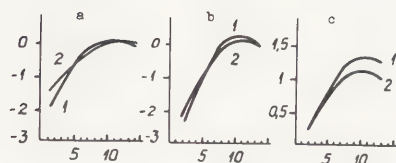


Fig. 2: Curves for gas exchange of *Chaetomium globosum*. Further on, same as in Fig. 1.

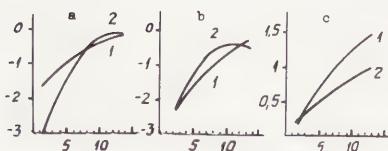


Fig. 3: Curves for gas exchange of *Trichoderma viride*. Further on, same as in Fig. 1.

Comparison between gas exchange of the fungi growing on laminated and nonlaminated paper showed that in the former case the curves as a rule pass at a lower level than in the latter. This phenomenon manifested itself most clearly in the respiratory quotient where the difference was much larger. The experiments revealed the following tendencies. One day after the paper samples with fungal spores were applied, oxygen consumption was found to be small. Carbon dioxide liberated in the form of traces. Two days after the experiment began, respiring intensity increased and was sufficient for quantitative analysis. The value of the respiratory quotient during this period appeared to be approximately the same in all cases and was about equal to 0.2. Further fungal growth revealed a sharp increase in the respiratory activity which began to decrease after 6-7 days. After 8-10 days carbon dioxide and oxygen content was stabilized, while the value of the respiratory quotient reached unity and continued growing.

Data of investigation of the infrared absorption spectra are given in Fig. 4. These spectra did not reveal radical differences between laminated and original paper for affected samples. In the spectrum of cotton paper (3) with fungal colonisation there were two characteristic lines 1640 cm^{-1} and 1740 cm^{-1} due to the presence of C=O bonds in the carbonyls and carboxyls. These lines were caused by the presence of the fungus biomass and are quite pronounced in its absorption spectrum (1). After the affected sample was treated with alkali, most of the fungal biomass passed into the solution which caused a sharp decrease in the peak amplitude on the alkali treated samples (5). Investigation of the laminated paper samples revealed similar results. The spectrum of affected laminated paper (4) also showed lines 1640 and 1740 cm^{-1} , but of somewhat smaller amplitude than in the original sample (3). After the affected sample of laminated paper was treated with alkali, these lines almost disappeared (6). Thus results of investigation of the infrared absorption spectra revealed small quantitative differences due to the lamination. Lines 1640 and 1740 cm^{-1} on the laminated paper samples had an amplitude equal to 75% of similar amplitudes of the same lines on the original fungi damaged samples.

Changes due to species differences among the fungi were also established in the experiments. The alkali-soluble fraction of the paper samples determined after a 13-day incubation revealed differences among the fungi in question. The results obtained were fairly well correlated with values of the respiratory quotients during the same period and are given in the table below. Maximum values were found in the experiments with *A. terreus* and minimum values, with *T. viride*.

Values of alkali-soluble fraction of paper samples and respiratory quotient of fungi by 13th day

Fungus	Alkali-soluble fraction, %	Respiratory quotient
<i>A. terreus</i>	21.4	1.5
<i>C. globosum</i>	1.2	18.4
<i>T. viride</i>	1.04	14.7
Control	-	1.55

Results of the experiments obtained lead to the following conclusions. Lamination of paper with a polyethylene film inhibits fungal growth. This effect, however, is not significant to consider lamination to be suitable for protection of paper against

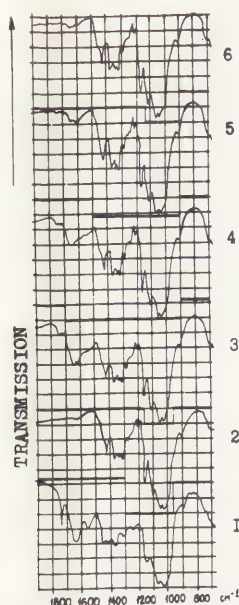


Fig. 4: IR-absorption spectra of the biomass of *Chaetomium globosum* (I) and different paper samples (2-6).

Abscissa - wave number, cm^{-1} . Ordinate - relative transmission.

2 - control paper; 3 - paper after fortnightly colonial growth; 4 - laminated paper after fortnightly colonial growth; 5 - same as 3, but after alkaline treatment; 6 - same as 4, but after alkaline treatment.

fungi damaging. Scanning electron photographs of the laminated-paper surface reveal holes with a diameter much larger than that of the fungal hyphae and spores. The differences in the fungal respiratory exchange on lamination and original paper observed in the experiments are, therefore, due to barrier role on the polyethylene for the gases evolve. This conclusion is confirmed by results of the infrared spectrophotometry which do not show qualitative differences in absorption spectra of the affected laminated and nonlaminated paper.

Quantitative characteristics of the fungal respiring activity can be measured even on the second day after the inoculation. During this period visual manifestations of the colonial growth are absent. The fungal growth can be found only by microscopic investigation with differential staining. The respiratory quotient appears to be the same for fungi of all species studied and is equal to 0.2. This factor is, therefore, a sufficiently sensitive indicator of fungal growth during an early period. At early stages of fungal growth the value of the respiratory quotient indicates that the main portion of consumed oxygen is expended for metabolic synthesis. On about the seventh day the respiratory quotient reaches unity and continues growing. This takes place due to a significant destruction of the substrate and formation of readily assimilable, which leads to enhanced liberation of carbon dioxide at the expense of the glucose splitting. The respiratory quotient also indicates uniquely the definite inhibition of fungi growth with polyethylene which cannot be assessed with certitude from determination of oxygen and carbon dioxide.

The results obtained show that polyethylene-lamination is not suitable for protecting paper against fungal damaging. Improvement in the various parameters of laminated-paper samples compared with nonlaminated ones does not exceed 30%.

This work was performed with paper samples laminated shortly before the experiments. It is undoubtedly interesting from the practical point of view to study the paper laminated with polyethylene film several years or decades ago. There is every reason to believe that susceptibility of the polyethylene film to fungal damaging will increase with time.

It follows, then, from objective criteria that application of polyethylene on document lamination does not provide bioproofness in storage.

References

1. Analytical infrared spectroscopy; fundamentals, techniques, and analytical problem-solving/ A.L. Smith. New York, etc.: Wiley, 1979. 322 p.
2. Kasparov S.V., Panikov N.S. Metodicheskiye aspekty issledovaniya gasoobmena v sisteme pochva-atmosfera // Vzaimodeistviye pochvennogo i atmosfernogo vozdukh: Ucheb. posobie / MGU im. M.V. Lomonosova. M., 1985. S. 47-62.
3. Kerner-Gang W. Massnahmen zur Bekämpfung von Mikroorganismen an Archivalien // Proc. 4th Intern. biotecn symposium. Berlin, 1978. S. 9-14.
4. Kestelman V.N., Yarovenko V.L., Melnikova E.I. The corrosion of polymeric materials under the conditions of the microbiological synthesis of enzymes // Intern. biotecn bull. 1972. Vol. 8, N 1. P. 15-19.
5. Miles J., Eggins H.O.W. Growth of thermophilic fungi on oxidation products of polyethylene // Ibid. 1970. Vol. 6, N 1. P. 13-17.



RESUME

La restauration complète et les problèmes de conservation in loco des "Vues d'Italie", papiers peints en grisaille de Dufour et Leroy (1823) conservés au Palais d'Arco à Mantoue sont exposés dans ce travail après une étude approfondie de ces papiers peints, de leur technique de fabrication, de leur état de conservation et des anciennes restaurations.

La restauratrice, en accord avec l'Opificio delle Pietre Dure, a établi une méthodologie particulière, individualisant tout d'abord des critères de base pour le choix des matériaux et pour la technique de montage.

Le choix s'est porté sur un entoilage au moyen d'une toile synthétique polyester et de deux adhésifs composés Glutofix 600 et Plextol D (41), entoilage qui sera fixé au mur au moyen de bandes de Velcro et de barettes de bois.

Les matériaux et la technique choisis dans ce travail ont permis de garantir la réversibilité, l'aspect original des papiers peints et la conservation pour laquelle nous proposons des interventions ponctuelles et une grande surveillance, vu l'impossibilité d'intervenir sur la structure du Palais d'Arco, monument historique. Ce travail étant encore en cours, la réinstallation des papiers in loco est présentée comme un projet, qui sera réalisé d'ici la fin de l'année 1987 sous la direction de la Surintendance aux Biens Artistiques de Mantoue et en collaboration avec la Fondation d'Arco.

RESTAURATION ET CONSERVATION DES "VUES D'ITALIE", PAPIERS PEINTS EN GRISAILLE DE DUFOUR ET LEROY (1823) CONSERVES AU PALAIS D'ARCO A MANTOUE

Nathalie Ravanel
Restaurateur privé
Via San Niccolò 107
50125 Florence, Italie

Cristina Danti
Inspecteur, historien d'art
Opificio delle Pietre Dure e Laboratorio di Restauro
Via degli Alfani 78
50121 Florence, Italie

Description des papiers peints

Les papiers peints du Palais d'Arco à Mantoue, salle dite de "Andreas Hofer", appartiennent à la série des "Vues d'Italie et de la Baie de Naples" de Dufour et Leroy; ils ont été exécutés sur les dessins de Prévost. Ces panoramiques en 'grisaille' avec rehauts d'ocre représentent : Amalfi, le Vésuve, les Bateaux à l'ancre, les Cascades, les Ruines Antiques... Des panneaux de plus petites dimensions représentent des paysages dont les sujets sont identiques deux à deux.

La composition des différents lés de ces panoramiques ne correspond pas exactement à la description du catalogue de Dufour car ils ont été recoupés et recomposés différemment pour être adaptés aux dimensions des murs.

Au-dessus des panoramiques et sur les quatre murs court une frise décorée de motifs de hiboux.

Le plafond est composé d'une seule toile (42,5 m²) tendue le long des bords sur des poutres de bois, poutres fixées sous le plafond à caissons. Sur la toile, couverte d'une première couche de papier, sont encollées des frises décoratives sur tout le pourtour; dans les angles sont appliqués des triangles de papier à l'intérieur desquels sont collés des motifs de grappes de raisins.

Technique de fabrication

Ces papiers peints ont été réalisés en xylographie. Sur un fond uniformément préparé et coloré, l'impression était faite, non plus à l'huile mais avec des couleurs épaisses à la détrempe, procédé connu depuis longtemps des chinois. Papillon (1698-1778) l'avait expérimenté puis abandonné car il craignait que les couleurs ne résistent pas à l'humidité, en particulier au moment de l'encollage et du montage.

Réveillon (1765-1789) utilisa la fabrication du papier vélin, l'encollage des feuilles en rouleaux de 9 aunes (10,70 m) et l'impression à la frappe au moyen d'un maillet de bois, le papier étant placé sous la planche.

Pour les panoramiques, le papier était préparé de la façon suivante : un fond de colle animale rendue épaisse avec du Blanc de Meudon était étendu sur le papier au moyen de pinceaux (opération appelée "fonçage") sans procéder au "lissage"; c'est pourquoi nous pouvons remarquer les traces laissées par le pinceau.

Les panoramiques étaient imprimées lé par lé avec des planches de petites dimensions (± 43x54 cm). Chaque couleur avait besoin d'une planche. Nous pouvons donc imaginer le nombre incalculable de planches nécessaires pour imprimer l'ensemble des panneaux.

Les couleurs à base de terres, opaques et denses, étaient préparées avec de la colle animale ou de l'amidon. La pauvreté du liant dans la préparation du pigment peut provoquer la chute de ce dernier, problème que nous retrouvons souvent dans les papiers de Dufour et que nous avons également observé dans les papiers du Palais d'Arco. Ces couleurs sont cependant très résistantes à la lumière.

Pour faire coïncider de manière parfaite les différentes planches, des marques étaient tracées sur les bords, marques que nous avons retrouvées sous les bords décoratifs. Les joints entre une planche et une autre étaient retouchés au pinceau.

Etat de conservation

Les différents panneaux se présentaient dans un très mauvais état de conservation, état imputable à plusieurs facteurs : la longue exposition à la poussière et à la suie de la cheminée, la situation climatologique inadaptée avec des écarts importants de température et d'humidité, les infiltrations d'eau par le toit, les anciennes restaurations, la négligence de l'homme et le montage inadapté.

Les panneaux étaient mis en place de la façon suivante : des bandes de toile (lin et chanvre) étaient collées et clouées sur le mur sur tout le pourtour de chaque panneau ; les panneaux étaient directement collés au mur et sur ces bandes de toile qui renforçaient les bords. Le papier s'étant décollé du mur, mais non pas des supports de toile, il en est résulté des tensions différentes dans le montage et des déchirures parfois très importantes. Les clous ont transféré des taches de rouille sur le papier, la toile et la peinture murale découverte sous les papiers peints ont laissé leurs empreintes sur la couleur.

La superficie du papier est devenue irrégulière ce qui a permis à la poussière de se déposer plus facilement.

Sur les papiers peints nous pouvions observer les dommages suivants :

- des taches d'humidité, nombreuses et étendues, en particulier sur les panneaux du mur extérieur où les infiltrations du toit ont été plus importantes et où s'est probablement manifesté le problème de la condensation. Sur ces panneaux nous observons de grandes pertes de papier et de couleur laquelle est devenue très fragile par suite de la disparition de l'adhérence. Certains panneaux étaient ainsi devenus presque illisibles. Le papier était lui même devenu très fragile et presque "désintégré" ;
- de nombreuses déchirures, parfois très étendues (voir panneau principal "les Bateaux à l'ancre", déchiré en deux parties dans le sens vertical, figg. 1 et 2) ;
- de nombreux trous dûs à des pertes de papier ou à la présence de pivots et du plâtre appliqué pour les fixer (certains pivots soutenaient une ancienne installation de sonnette, d'autres des cantonnières autour des fenêtres...) ; des trous dûs aussi à la nouvelle installation électrique fixée directement sur les papiers peints (mur extérieur) ;
- des pertes de couleur nombreuses et étendues, dues à des abrasions, aux infiltrations et à la perte de cohésion de la couleur elle-même qui se brise et se pulvérise ;
- quelques taches de substances grasses, en particulier sur le panneau situé au-dessus de la cheminée ; des traces de chaux utilisée probablement pour repeindre le plafond et des traces de scotch autour de certaines déchirures ;
- autour de la porte de passage entre la salle et la cuisine du Palais, présence de suie qui se gommait difficilement.

Précédentes restaurations

Presque tous les panneaux portent les signes d'une plus ou moins ancienne restauration.

Certains panneaux ont été détachés du mur (panneaux situés au-dessus des portes), entoilés et restaurés complètement avant d'être reclusés directement sur le mur.

D'autres panneaux ont été restaurés sur place : déchirures et lacunes ont été recollées avec du papier kraft et du papier Miliani de couleur grise à l'aide de colle forte animale ; certains, par endroits, ont été recollés directement sur le mur avec du Vinavil fixés avec des clous. L'usage du Vinavil et la 'fraîcheur' de la colle animale nous fait penser à une restauration assez récente.

Les anciennes retouches ont été exécutées à la détrempe, recouvrant en de nombreux endroits la couleur originale.

Premières interventions

Après avoir examiné l'état de conservation de l'ensemble des papiers peints, nous avons décidé de procéder à une restauration complète.

Nous avons tout d'abord préparé la documentation de la disposition des différents panneaux sur les murs pour permettre leur remontage exact après la restauration.

Le démontage a été fait de la façon suivante :

La superficie des papiers peints a été dépoussiérée au pinceau. Les points faibles et pulvérulents de la couleur ont été fixés à l'aide de méthylcellulose (Glutofix 600, Kalle) à 1%. Les papiers ont été détachés à l'aide de scalpels et de spatules en acier, ainsi que de tuyaux en plastique de large diamètre (14 cm) pour enrouler au fur et à mesure les plus grands panneaux et les frises. Nous avons ensuite nettoyé le verso de tous les panneaux pour éliminer les traces de plâtre et de colle avec des scalpels et du papier de verre ; le recto a été dépoussiéré de nouveau avec des gommes de différentes duretés.

La toile de fond ayant perdu toute cohésion et résistance était inutilisable pour la nouvelle restauration et a été découpée le long des bords et enroulée au fur et à mesure sur des tubes en plastique. Les frises et les angles imprimés collés sur la toile ont été décollés ; recto et verso ont été nettoyés à sec.

Le premier nettoyage a rendu le papier plus élastique et a donc permis d'enrouler les différents panneaux et les différentes frises sur ces mêmes tubes en plastique en protégeant chaque partie avec du papier vélin.

Les deux plus grands panneaux ont été décollés et divisés chacun en trois parties à la jonction des lés pour faciliter le transport, transport effectué du Palais d'Arco au laboratoire de restauration à Florence.

Restauration

Ce travail d'une dimension exceptionnelle (63 m² pour les papiers peints et 42,5 m² pour le plafond) avait besoin pour être affronté d'un projet particulier, rarement rencontré dans la bibliographie existante.

Nous avons d'abord individualisé les critères de base pour le choix des matériaux et pour la technique de montage qui devront tenir compte des facteurs suivants :

- la qualité et la résistance des matériaux aux micro-organismes et aux insectes ; la résistance à la lumière, à la différence de température et d'humidité ; la résistance au feu ;
- la réversibilité et la non-adhérence complète au mur ;
- le respect de l'aspect original des "papiers peints" ; nous devions donc écarter le montage sur cadre dont l'épaisseur aurait complètement transformé l'apparence générale ;
- la légèreté des matériaux et leur manipulation facile (vu les dimensions des panneaux) ;
- le coût de la restauration par rapport à l'oeuvre.

Pour respecter ces normes, nous avons décidé l'entoilage complet de tous les panneaux avec une toile synthétique polyester (Ballerini Filtrazioni, Milan) et un adhésif composé, formé de méthylcellulose (Glutofix 600, Kalle) et d'un copolymère acrylique-méthacrylique (Plextol D 541, Röhm), la toile étant ensuite remontée avec des bandes de velcro, procédé invisible et réversible.

Le choix de la toile s'est basé sur les qualités suivantes :

La bonne résistance à la traction, la bonne récupération élastique, une hygroscopie basse 0,4% (le coton 20%), une bonne résistance aux acides organiques et inorganiques et aux alcalis, l'insensibilité aux micro-organismes, la résistance à la lumière et, enfin, la résistance à la chaleur ; en effet, la toile polyester fond à 250-255°, d'autre part elle est autoextinguible ; le coton brûle à 150° et n'est pas autoextinguible.

Quant à l'adhésif, nous avons choisi de composer deux adhésifs originaux qui nous ont permis d'obtenir les caractéristiques suivantes : une plus forte adhérence et résistance aux micro-organismes données par le Plextol ; la réversibilité et une plus grande viscosité assurées par la méthylcellulose.

Vu l'état de porosité des papiers, porosité due en grande partie au contact prolongé avec le plâtre, nous avons décidé d'imperméabiliser en quelque sorte le verso en vaporisant une solution d'hydroxylpropylcellulose (Klugel G, Hercules) à 1,5% dans l'alcool éthylique.

La restauration elle-même a commencé par un nouveau nettoyage du verso, à sec et par humidité capillaire pour éliminer les traces de colle ; le nettoyage du recto a été exécuté à sec et après avoir décollé le bord décoratif et les différents lés de chaque panneau en procédant par humidification sur le verso, le nettoyage a été complété lé par lé par vaporisation d'une solution d'eau déionisée et d'alcool éthylique en absorbant l'excédent avec du papier buvard. Une fois nettoyé et sec chaque lé a été imperméabilisé avec la solution d'hydroxylpropylcellulose citée ci-dessus.

Nous avons alors encollé les déchirures et restauré les lacunes avec du papier japonais.

Certaines zones de couleur ont été fixées avec une solution de Klugel G à 1% dans l'alcool éthylique.

Les panneaux les plus fragiles ont été doublés de papier japonais. L'entoilage a été exécuté de façon traditionnelle mais sur un support vertical qui permettait de respecter la technique originale des papiers peints et qui facilitait le travail.

Sur le support de bois ont été appliqués des feuilles de papier au silicone pour éviter que le montage ne se colle au support. La toile a été alors tendue sur le support et une épaisseur de papier japonais a été encollée avec l'adhésif composé que nous avons choisi. Nous avons individualisé pour ce travail deux

composés différents, le premier appliqué sur la toile contenant plus de Plextol (1 part de Plextol D541, 1 part de Glutofix 600 à 4,5% et 1 part d'eau déionisée) et le second en contact avec l'original et contenant plus de metylcellulose (1 part de Plextol D 541, 2 part de Glutofix 600 à 4,5% et 1 part d'eau déionisée).

Lorsque l'ensemble a été sec, nous avons collé les papiers peints lé par lé après les avoir humidifiés, l'adhésif étant étendu sur le papier japonais. L'application s'est terminée à l'aide d'un rouleau de caoutchouc passé sur la superficie.

Les lacunes ont été restaurées avec du papier japonais. La re-touche picturale a été exécutée avec différents types de couleurs : des crayons Conté, des pastels et des aquarelles. Nous avons délibérément écarté les couleurs à la détrempe, peu stables. Les retouches aux pastels et aux crayons Conté ont été fixées avec la solution de Klugel G à 1% dans l'alcool éthylique.

Les panneaux ont été détachés du support de bois.

Un ruban de velcro a été cousu avec du fil polyester sous les bords latéraux et inférieurs utilisant une machine à coudre électrique et un point en zig-zag pour assurer la stabilité.

Le bord décoratif a été recollé avec le même ruban adhésif utilisé pour l'entoilage (fig. 3).

Projet de réinstallation sur place des panneaux et du plafond

Avant de remonter les panneaux, les murs seront nettoyés des vieux clous et pivots ; l'installation électrique sera fixée dans le mur ; les trous plâtrés et les irrégularités planifiées. Le mur extérieur sera asséché et assaini sans détruire le plâtre existant sur lequel nous avons découvert une peinture murale qui sera conservée intacte.

Dès que la salle sera en état et dès la fin 1987, les papiers peints seront remontés de la façon suivante :

Les bords des panneaux recouverts par d'autres panneaux ou par les poutres supérieures et les frises seront directement cloués sur des baguettes de bois, elles-mêmes vissées dans le mur. Les bords supérieurs des panneaux seront encollés sur le bord de la frise supérieure selon la position originale de l'ancien montage. Pour les bords externes et visibles, nous visserons dans le mur des baguettes de bois sur lesquelles sera fixé le second ruban de Velcro. Les panneaux sur lesquels a été cousu le premier ruban de Velcro pourront ainsi être réinstallés sur le mur au moyen d'une technique invisible et complètement réversible. De plus, l'utilisation des baguettes de bois permet d'obtenir un espace entre le mur et les papiers peints.

Normes de conservation

Ces papiers peints étant conservés dans la structure même d'un palais ancien, le Palais d'Arco, nous ne pourrions pas procéder à des transformations radicales et à de gros travaux de modernisation. Nous proposons donc de petites interventions ponctuelles pour améliorer les conditions climatiques et pour assurer la protection des papiers.

Des interventions devront être faites sur les fenêtres pour en améliorer la fermeture et pour limiter le passage de la lumière; sur la cheminée qui devra être hermétiquement fermée. L'illumination de la salle sera contrôlée ainsi que les conditions thermohygrométriques qui seront enregistrées et au besoin sur lesquels il faudra intervenir en utilisant un humidificateur ou un déhumidificateur selon les besoins. En outre, le toit sera contrôlé périodiquement pour prévenir l'éventualité de nouvelles infiltrations. Enfin, nous suggérons que les visites soient réglementées dans le temps et dans le nombre de personnes.

Bibliographie

Polyester

- Polyester Sailcloth fabric : a high-stiffness lining support, G. Hedley and C. Villers ; in Science and Technology in the Service of Conservation, Washington Congress, IIC, sept. 1982.
- Matthews' Textile Fibers, Herbert R. Mauersberger ; John Wiley & Sons, New York, 1954.
- Identification of Textile Materials, The Textile Institute, Manchester, Grande Bretagne 1965.
- Nuovo Dizionario Merceologico, Villavecchia Eigenmann, vol. III Ed. Hoepli, 1976.

Adhésif

- Further Developments in cold-lining (Nap Bond System), U.R. Mehra; ICOM Congress, Venice, 1975.
- Adhesives and Coatings, Science for Conservators, Book 3, 1984.

Grandes dimensions

- The Treatments of Oversize Paper Artifacts, Gary E. Albright, Thomas K. McClintock.
- The Conservation of a 17th Century Outsized Map, E.D. Bosshard; ICOM Congress, Zagreb, 1978.

Papiers peints

- Trois siècles de Papiers peints, Musée des arts décoratifs, Paris, 1967.
- Histoire du Papier peint en France, préface par Jean Bourguignon, Ed. d'Art Charles Moreau, Paris, 1935.
- Wallpapers in Historic Preservation, C. Lynn Frangiamore, Washington D.C. 1977.
- Wallpaper in America : the Seventeenth Century to World War I, Catherine Lynn, New York, the Bana Foundation and the Cooper-Hewitt Museum, 1980.
- Nouveau manuel complet du Fabriquand de Papiers peints, Sébastien Lenormand, 1830.
- "Sauvages de la Mer du Pacifique", Treatment of an Early 19th Century Wallpaper Depicting the Voyages and Death of Captain Cook, M. Wood Lee, K. Rachmann, S. Fletcher ; Preprints Congress, 1977.
- Conservation within Historic Buildings, Publ. IIC, IIC Vienna Congress, sept. 1980.
- Conservation of Historic Wallpaper, Andover, Mass. 1980.

Musée du Papier Peint, 28 rue Zuber, 68170 Rixheim, France
(Département du Musée de l'Impression sur étoffes,
3 rue des Bonnes Gens, 68100 Mulhouse, France).

Les auteurs remercient la Surintendance aux Biens Artistiques de Mantoue, la direction et le personnel de la Fondation d'Arco à Mantoue pour leur aimable et active collaboration.

Fig.1 :

Fig.1

C1 et C3: panneaux plus petits situés au-dessus des portes. Ces panneaux ont été complètement restaurés et réentoilés au cours d'une ancienne restauration puis reclusés directement sur le mur.
 C2: les Bâteaux à l'ancre, le panneau le plus grand de la série, composé de 9 lés (4,20m x 2,65m). Le papier peint était déchiré en deux parties dans le sens vertical puis successivement recollé avec du Vinavil et reclusé au mur.
 C4, C5, C6: trois bandes de papiers peints qui composent la frise supérieure. C4 et C6 sont de couleur uniforme et C5 est décorée avec des motifs de hiboux. Cette frise est elle aussi déchirée en correspondance de la déchirure du panneau principal. En certains endroits la couleur a perdu toute cohésion et devra donc être fixée.

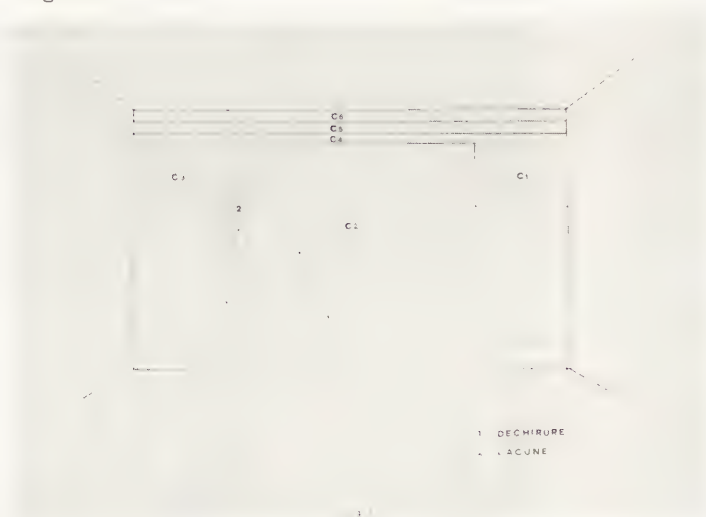


Fig.2

panneau C2 après la dépose, la division en 3 parties à la jonction des lés et avant la restauration.

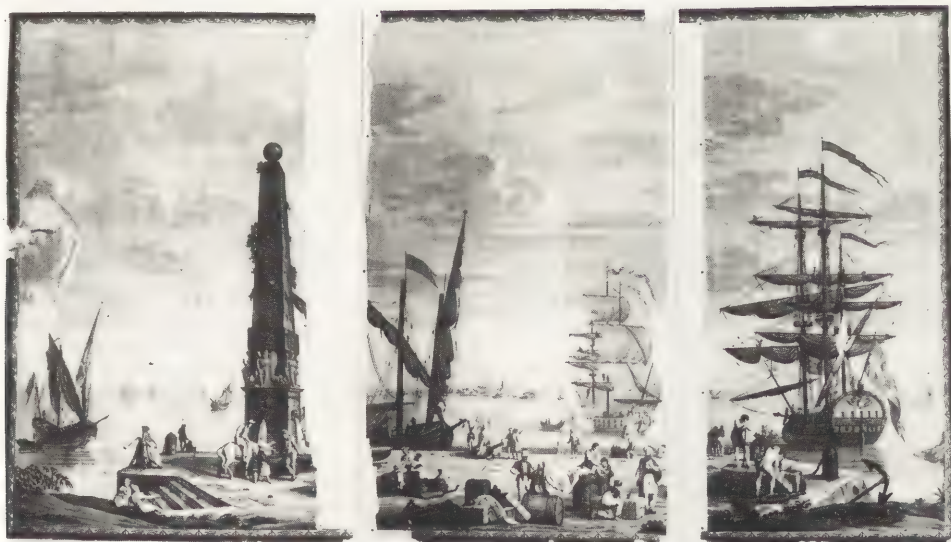


Fig.2

Fig.3

Panneau C₂ après la restauration,
avant la réinstallation sur place.

Fig.3



Dessin au trait : Andrea Crescioli

Documentation photographique : Sergio Cipriani

SUMMARY

For the comparative study into the possibilities and limits of various analytical methods test material was prepared from a well known dyestuff. This material was given to each researcher to test his or her method. Particular attention was given to the question of minimum sample quantity necessary for positive identification.

THE ANALYSIS OF NATURAL DYESTUFFS AND ORGANIC PIGMENTS:
A COMPARATIVE STUDY INTO THE POSSIBILITIES AND LIMITS OF
VARIOUS METHODS

Wilma G.Th. Roelofs, Pieter B. Hallebeek, Judith H. Hofenk de Graaff, Riet F.S. Karreman
Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1075 EA Amsterdam, The Netherlands

Introduction

For the identification of natural dyestuffs in ancient textiles and organic pigments on e.g. illuminated manuscripts several methods are used (1, 2, 3, 4). Natural dyestuffs and organic pigments are basically similar metal complexes made of chemical compounds from plants or animals and a metal e.g. aluminium, tin, iron, etc.

Consequently the analytical methods used for the identification are similar. Generally chromatographic and spectroscopic methods are used.

When which method is used for the identification is often arbitrary and depends on the experience of the researcher and the availability of the equipment.

Without being detrimental to the quality of researcher or equipment it seems useful to compare various methods and investigate their possibilities and limits.

Starting point for this research was the preparation of test material from a well known and much used dyestuff.

This test material was made available to each researcher in order to test his or her specific method.

The foreknowledge of the ingredients used and the quantity of the specific constituents in the test material made it possible to calculate the minimum quantity of sample material necessary for a positive identification.

The test material was already given to a number of colleagues from other institutions, and it is still available for those researchers who are interested to participate in this research program.

The methods under investigation could be:

- chromatographic methods
- spectroscopic methods
- combinations of the abovementioned methods
- Raman microprobe
- X-ray diffraction
- atomic absorption spectrophotometry

From the available methods and equipment in the Central Research Laboratory the following methods were chosen:

- Thin Layer Chromatography (TLC)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Combinations of TLC and FTIR
- Flameless atomic absorption spectrophotometry (FAAS)

Reason for this were:

Already existing TLC separation systems for dyestuffs and much experience in this field; promising preliminary results with combinations of TLC and IR.

After the first experimental work the laboratory obtained a new Fourier Transform Infrared Spectrometer with new potentialities. The research was therefore continued with FTIR.

For the metal content the FAAS was the only method available to carry out the quantitative analysis of the metal part in the organic complex and to calculate in this way the detection limits in relation to the sample size.

Choice of the test material

As already mentioned in the introduction the material used for the comparison of the various analytical methods should consist of one particular dyestuff which has been used frequently both as a dyestuff and as a pigment (5).

Madder (*Rubia tinctorum*) seems to fulfill this aim because it:

- has been used as a dyestuff and as a pigment
- is still available nowadays
- ancient recipes are available
- chemical composition is known
- methods for identification are known
- several metals are used to form complexes.

Preparation of the test material

Madder root (*Rubia tinctorum*) with the main components alizarin and purpurin was used for dyeing wool and silk and to prepare the pigment "madder lake".

Basically the dyeing procedure is that of a 17th century Dutch recipe (6). It is, however, difficult to repeat the exact procedure because of the quantity of sample material. Another reason is that the chemicals used as e.g. mordants and other auxiliaries are often much purer than the ingredients used in the past.

Because of this a recipe from a contemporary dyebook was finally chosen, which was similar to an ancient recipe (7).

For the practical dyeing procedure laboratory equipment was used. In the dyeing procedure the bath ratio was 1:50. The amount of mordants and dyestuffs were calculated on the dry weight of the textile material.

Wool and silk were mordanted with the following chemicals:

1. 20 % alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$)
2. 20 % alum + 5 % cream of tartar ($C_4H_5KO_6$)
3. 8 % iron(II)sulphate ($FeSO_4 \cdot 7 H_2O$)
4. 4 % tinchloride ($SnCl_2 \cdot 2H_2O$) + 12,5 % cream of tartar

All the mordants are of a technical quality to approximate the ancient materials.

Wetted wool is placed in the cold mordant bath and the temperature is slowly increased to 90°C. and kept there for 1.5 hours. Then the yarn is taken from the mordant bath, squeezed out, rinsed in tap water and dried. The dyeing procedure is carried out the next day. For the dyeing procedure 100 % madder root (calculated on the weight of the textile material) was powdered and mixed with a small amount of tap water and boiled for a short time.

After boiling the mixture is diluted with cold tap water to the calculated amount necessary for the dyeing. The temperature is increased to 40 - 50°C. The wetted and mordanted wool is added to the dye bath and the temperature increased to 70 - 80°C. This temperature is kept for 1.5 hours. The dyed wool is cooled down in the dye bath. Then the wool is rinsed in tap water. After rinsing the dyed material is boiled with 2 % Marseille soap for ten minutes, rinsed and dried.

For the preparation of madder lake a modern interpretation of a mediaeval recipe (8) was used. In this recipe dyed wool is cut into small pieces and boiled with woodash (K_2CO_3) and precipitated with a solution of alum.

For the preparation of the test material the above described dyed wool, mordanted after no. 1 is used. The wool (ca 20 g.) is cut into small pieces and boiled with 200 ml 20 % K_2CO_3 . Because of the alkalinity most of the wool is degraded and dissolves almost completely in the potassium carbonate solution. After boiling 10 % alum solution is added to precipitate the lake. The precipitate is filtered off, rinsed and dried. After drying the pigment is ground and mixed with the binding medium eggwhite.

Pigment with binding medium were applied to new ragpaper and parchment.

Investigations

Thin Layer Chromatography (TLC)

TLC has proved to be an excellent separation technique for the identification of natural dyestuffs. The methods used in this research are those described by Roelofs and Hofenk de Graaff (2). In order to determine the detection limits samples of a mixture of pure alizarin and purpurin (1 : 1) and of all the dyed materials were analysed. All components became clearly visible after detection. Additional to the two spots of alizarin and purpurin, two extra spots became visible. These have not yet been identified but will be analysed in a future study.

To calculate the detection limit for the chromatographic system a chromatogram was made with different quantities of alizarin and purpurin. To this purpose 0.81 mg alizarin and 0.78 mg purpurin were dissolved in 25 ml methanol. From this solution quantities of 0.2 - 0.5 µl were applied to the thin layer plate.

An amount of 0.20 µl of the mixture (= 6.4 ng of the individual compounds) was still visible after detection. Starting from the theoretical assumption that in madder the ratio of alizarin and purpurin is 1 : 1 and the knowledge that the quantity of dyestuff on the fibre in most cases does not exceed 5 % and the mordant content is appr. 10 %, 300 ng of a textile sample is the minimum quantity necessary for a positive identification of the dyestuff. This theoretical calculation is proved in the practical application. In this application the routine procedure was followed for the analysis of dyestuffs and pigments. A chromatogram was made with various amount of fibres. After detection it became clear that 1 fibre of wool with a length of 1 cm (0.4 µg) was necessary for a positive identification.

For the identification of the madder lake pigment the same procedure was followed. In this case a sample of 0.5 μg was necessary for positive identification.

Fourier Transform Infrared Spectroscopy (FTIR)

Although infrared spectroscopy has proved its usefulness in the analysis of small quantities of materials, FTIR is a new development which does increase the sensitivity and resolution considerably. The amount of sample necessary is reduced and through combinations of new technology the FTIR is made into an infrared microprobe.

The computer which is part of all FTIR instruments has had quite an impact on the technique.

One of the obvious computer applications is taking a solvent out of a spectrum by running the spectrum of the sample and the spectrum of the pure solvent and subtracting the spectra.

Another useful application is spectrum stripping. When in a complex mixture one of the constituents is recognized the spectrum of the pure constituent can be subtracted and scaled so that some recognizable feature of its spectrum has the same intensity as in the original spectrum and remove the contribution of that component from that spectrum.

Another feature is the possibility of blowing up parts of a spectrum so that specific absorption bands of small constituents become visible. In the investigation of the very complex samples from objects of art these features become very useful (9).

The instrument

Perkin Elmer, model 1750 FTIR spectrometer comprises an optical module, electronics, model 7300 professional computer and CDS-3 applications software.

The model 1750 is a single beam FTIR spectrometer using an improved Michelson interferometer which compensates for any dynamic misalignment. The KBr beamsplitter gives a frequency range of 4000 to 400 cm^{-1} . The interferometer alignment is achieved by a servo system.

The source and detector are actively stabilised. The standard resolution is 1 cm^{-1} to 64 cm^{-1} .

The sample compartment is flushed with dry air for reducing atmospheric water in the sample area. The professional computer is used for full instrument control and data handling.

Experimental

Reference spectra were made of the pure components alizarin and purpurin. Because of the small quantities in real samples the micro-pellet of 1.5 mm was chosen for all the experiments.

In 1600 ng of a mixture of alizarin and purpurin (1 : 1) both components could be identified separately (Fig. 1).

0.5 mg of a wool sample dyed with madder on an alum mordant (no 1) was hydrolysed with 10 % hydrochloric acid, the dyestuff was extracted with methanol and the dried extract was mixed with potassium bromide. The spectrum was very difficult to interpret. Alizarin and purpurin could not be identified. This was caused by a relatively large quantity of protein remainders, originating from the wool which disturbed the spectrum. Even using a reference spectrum of wool and subtraction of the two spectra no identifiable spectrum was obtained.

A sample taken from the madder lake pigment was mixed with potassium bromide. The spectrum was compared with a reference spectrum of the binding medium (eggwhite). By subtraction of the two spectra and comparing the remaining spectrum with a reference spectrum the pigment could be identified positively (fig. 2-5). The minimum quantity of pigment was appr. 5 μg .

Conclusion

Even with the higher resolution FTIR is not the optimum method for the analysis of natural dyestuffs on textiles. With a pigment as madder lake e.g. on illuminated manuscripts the results are better but not optimum.

Combination of TLC and FTIR

Although FTIR has proved its sensitivity in the preliminary experiments the analysis of complex mixtures remains difficult because FTIR is not a separation technique. Especially for the identification of unknown components in a complex sample the combination with TLC has proved its usefulness.

In this combined procedure TLC was used as the separation technique and FTIR as the tool for the identification of the isolated constituents.

Experimental

Using TLC as separation technique and FTIR for identification of unknown components of a dyestuff a number of precautions have to be taken to prevent unnecessary disturbance of the spectra.

- the solvents of the eluent should be of analytical grade
- the TLC-plate should be prewashed several times with the eluent to remove all impurities.

For the separation of the constituents of an unknown dyestuff or organic pigment the sample is treated with 10 % hydrochloric acid to hydrolyze the metal part from the organic complex. After evaporation of the acid the dyestuff is dissolved in methanol. This solution is applied to the thin layer plate and the elution is carried out. After elution the separated spots or lines are scraped from the plate together with the adsorbent.

A glass tube with a length of 60-80 mm and a diameter of 1-2 mm, funnel - shaped and open at both ends is filled at one side with quartz wool (fig. 10).

The sample scraped from the TLC-plate is put into the glass tube. Another 10 mm of quartz-wool is placed on top of the sample. After that the rest of the glass tube is filled with finely ground potassium bromide. The glass tube is placed in a small tank with solvent (10).

The glass tube functions as a refinery where the mixture of the unknown component and the adsorbent is separated by means of column chromatography. The glass tube is placed in a solvent e.g. methanol or ether and after the elution the unknown component is concentrated in the top layer of potassium bromide. After drying it is then pressed into a 1.5 mm pellet and the spectrum can be run.

To test the above described technique experiments were carried out with a mixture of pure alizarin and purpurin 1:1.

As already calculated 800 ng of alizarin and purpurin were necessary to obtain a identifiable FTIR spectrum. Because of this 1600 ng of the mixture was applied to the thin layer plate in the shape of a line. After the elution one of the components is scraped from the plate and treated as described above and a spectrum is run.

To control the influence of the adsorbent on the spectrum of the unknown component the first is extracted with the solvent used. This extract is evaporated and mixed with potassium bromide. To control the effect of the separation by means of the glass tube the extract of the adsorbent is filtered in this way. From the two spectra it became clear that the extract through the glass tube was superior to the normal extract.

This experiments were carried out with two solvents: methanol and ether. In ether less disturbance from the TLC plate on the spectrum appeared (fig. 6,7).

Using the possibilities of the FTIR apparatus the spectrum of the TLC plate extract is subtracted from the spectrum of the unknown sample. In this way a much better spectrum is obtained and the identification on the unknown sample improved.

The experiments were carried out with alizarin and purpurin (fig. 8,9).

Flameless Atomic Absorption Spectrophotometry "FAAS"

Introduction

The major advantage of atomic absorption spectrophotometry is that it has no spectral and very few chemical interferences.

As chemical separations are not necessary the possibilities of FAAS for the determination of aluminium, tin and iron in textile mordants were investigated.

The purpose was to identify the mordants by means of the determination of the metal content.

In the past several methods have been used for the identification of metals on textiles such as chromatography, spectrophotometry, potentiometry.

These methods have all proven to be useful but they do possess certain disadvantages and limitations. Many ancient textiles contain finishes and residues of previous treatments, washing, bleaching etc. and these analytical schemes usually necessitate separation and removal of interfering substances.

The atomic absorption technique, on the other hand, involves only a single extraction of the fabric diluted to a known volume, injection of a fixed volume in the graphite oven and direct scale reading on the instrument (11, 12, 13).

The instrument

The instrument used was the PERKIN - ELMER model 303 atomic absorption spectrophotometer equipped with the heated graphite atomizer HGA - 70.

Through the new technique of flameless AAS using an electrically heated open graphite tube the researcher has the possibility of determining trace metals as low as 10^{-12} g. The principle of flameless AAS has been known for about 20 years. After a number of years of development the HGA - 70 appeared as a commercial instrument capable of determining trace metals in the range 10^{-9} g. to 10^{-12} g. on a routine basis. The HGA - 70 enables the essential steps of flameless AAS to be carried out in programmed form. The first stage is the drying of liquid samples. The HGA - 70 controls the drying through temperature and time. For aqueous solutions the drying time in seconds is 1.5 to 2 times the number of microliters injected. The second stage: the thermal destruction is not as unproblematical as the drying and atomization stages. With metal traces to be determined in varying amounts of accompanying material (organic, inorganic salts) the temperature has to be chosen very carefully with respect to the vapour pressure and atomization temperature of the metal.

The third stage is the actual atomization of the sample.

Principally the atomization temperature is higher than the temperature for the thermal destruction of the matrix. The normal sequence for the programming is:

- a) drying at a temperature of 100°C
- b) thermal destruction of the matrix, temp. 100°C - 1200°C
- c) atomization, temp. 1200°C - 2600°C.

Instrumental parameters :

	<u>Aluminium</u>	<u>Tin</u>	<u>Iron</u>
Lamp source (H. C. L.)	Al	Sn	Fe
Current (mA)	30	20	20
Wavelength (nm)	309	225	248
Thermal decomp. program	7	4	7
Atomization voltage	10	8	9
Purging gas : ARGON			

Experimental

Standard solutions of aluminium, tin and iron were prepared by dissolving the metal in hydrochloric acid. The solutions were calibrated to resp. 0.2 $\mu\text{g/ml}$ = ppm aluminium,
1.0 $\mu\text{g/ml}$ = ppm tin,
0.2 $\mu\text{g/ml}$ = ppm iron.

This solutions were used for comparison with the acid extractions of the test material.

0.030 g. of the test material was weighed and placed into a 10 ml beaker. 5 ml of 0.5 N hydrochloric acid was added and the temperature increased to just below boiling temperature.

This temperature was kept for 20 minutes. The solution was then transferred to a 10 ml volumetric flask, cooled off and diluted to the calibration mark with deionized water.

Each metal was determined by means of a injection of 10 μl of the prepared solution into the graphite oven. This was repeated 10 times for each sample.

The average value was compared with the standard curve of each of the three metals prepared by dilution of the stock solutions. For each metal a reference solution was prepared from hydrochloric acid and distilled water.

Comparative results of percent aluminium acid extraction technique.

1. 2.6 $\mu\text{g/ml}$ = ppm = 0.06% on weight of fabric
- 2a. 3.2 $\mu\text{g/ml}$ = 0.06% on weight of fabric
3. 0.6 $\mu\text{g/ml}$
- 4a. 0.8 $\mu\text{g/ml}$
- 4b. 0.8 $\mu\text{g/ml}$

Comparative results of percent tin acid extraction technique.

1. 0.8 $\mu\text{g/ml}$ = ppm
- 2a. 0.8 $\mu\text{g/ml}$
- 2b. 0.5 $\mu\text{g/ml}$
3. 0.6 $\mu\text{g/ml}$
- 4a. 2.1 $\mu\text{g/ml}$ = 0.04% on weight of fabric
- 4b. 2.5 $\mu\text{g/ml}$ = 0.04% on weight of fabric

Comparative results of percent iron acid extraction technique

1. 1.2 $\mu\text{g/ml}$ = ppm
- 2a. 1.6 $\mu\text{g/ml}$
- 2b. 1.6 $\mu\text{g/ml}$
3. 3.8 $\mu\text{g/ml}$ = 0.08% on weight of fabric
- 4a. 0.7 $\mu\text{g/ml}$
- 4b. 0.8 $\mu\text{g/ml}$

The relative standard deviation for aluminium determined directly in the extracted sample using appropriate standards was 6%, for tin: 8% for iron: 6%.

It is quite evident from the results presented that the flameless atomic absorption technique coupled with the aqueous acid extraction technique can be used quite effectively and with great rapidity for the determination of aluminium, tin and iron in textiles, related to the percentages that are released from the fibres by the acid treatment.

When the calculated percentages of the three metals are compared with the known detection limits which are for:

aluminium : 2×10^{-10} g.

tin : 2×10^{-8} g.

iron : 2×10^{-11} g.

It can be calculated that the minimum amount of textile sample required for a positive identification of the metal is for:

aluminium : 0.03 mg

tin : 0.07 mg

iron : 0.02 mg

For the analysis of the metal content in an organic pigment the test material "madder lake" was investigated.

Samples were taken from the following materials:

1. Parchment backside; reference
2. Parchment frontside with madder lake pigment
3. Ragpaper backside; reference
4. Ragpaper frontside with madder lake pigment
5. Madder lake pigment; reference

The preparation of the acid extraction was made in the same way as for the textile material.

Comparative results of percent aluminium acid extraction technique.

1. $0.5 \mu\text{g/ml}$ = ppm

2. $5.4 \mu\text{g/ml}$ = 0.10% on weight of the parchment

3. $0.2 \mu\text{g/ml}$

4. $4.8 \mu\text{g/ml}$ = 0.08% on weight of the paper

5. $15.6 \mu\text{g/ml}$ = 0.36% on weight of the pigment

Relative standard deviation for aluminium = 6%.

When for the identification of the metal of a mordant a qualitative measurement is sufficient it is possible to analyse a solid sample with FAAS.

In this case we need a single fibre with a length of 2 to 5 mm which is placed in the centre of the graphite oven.

The sample is atomized completely and we have a positive identification of the metal when present due to the fact that not only the extractable amount of metal but also the metal bound to the fibre is available for analysis.

In this case it is very important to make the right choice concerning temperature and time of the second stage, the thermal destruction of the fabric, because one has to be certain that all the organic material is ashed but below the atomization temperature of the metal.

Conclusion

Comparing the results of the various methods described the following conclusions can be drawn:

- For the analysis of natural dyestuffs and organic pigments thin layer chromatography has proved its usefulness. The minimum quantity of sample needed for a positive identification is appr. $0.4 \mu\text{g}$ of a textile (this is less than one fibre with a length of 1 cm) or $0.5 \mu\text{g}$ of a pigment. The needed quantity depends of course of the percentage dyestuff on the fibre which can vary from 0.5 - 5%. The calculated minimum in this research based on a percentage of 5%. The identification by means of thin layer chromatography can only give a positive answer when reference material is available.
- For the identification of an unknown dyestuff or pigment or an unknown component of these, the combination of TLC and FTIR has given good results. Especially the use of the filter tube for further purification of the sample gives a better possibility for identification. The minimum quantity needed depending of the percent of the unknown component in the dyestuff is at least 0.3 mg of a textile material or $3.2 \mu\text{g}$ of a pigment.
- Although FTIR is not the recommended method for the analysis of dyestuffs on textile material it can be used for the identification of an organic pigment by using the special techniques of the apparatus like subtracting and zooming of the spectra.
- For the identification of the metal part of a mordant dyestuff FAAS has proved to be a rapid and accurate method for as well the qualitative as the quantitative analysis.

For the qualitative identification only one fibre is needed. For

the quantitative analysis at least 0.02 - 0.07 mg of a fibre or a pigment is needed.

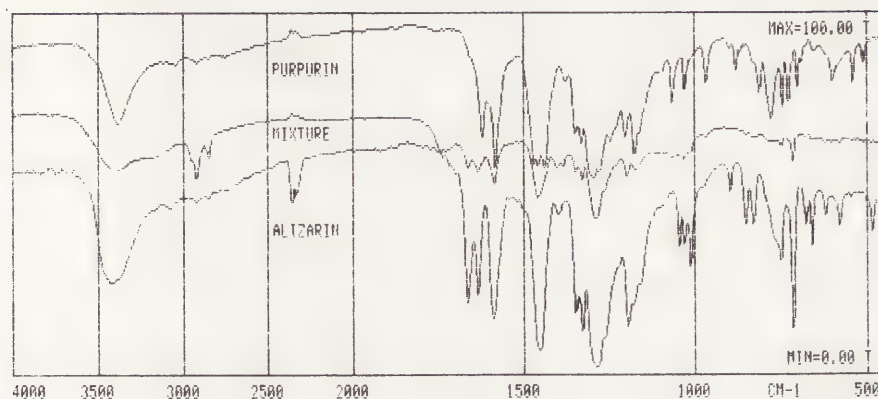


Fig. 1.
Spectra of alizarin, purpurin and the mixture of both.
The specific wavelengths for alizarin and purpurin in a mixture
are resp. 1664, 1634, 1010, 715 and 1621, 600, 540 cm⁻¹.

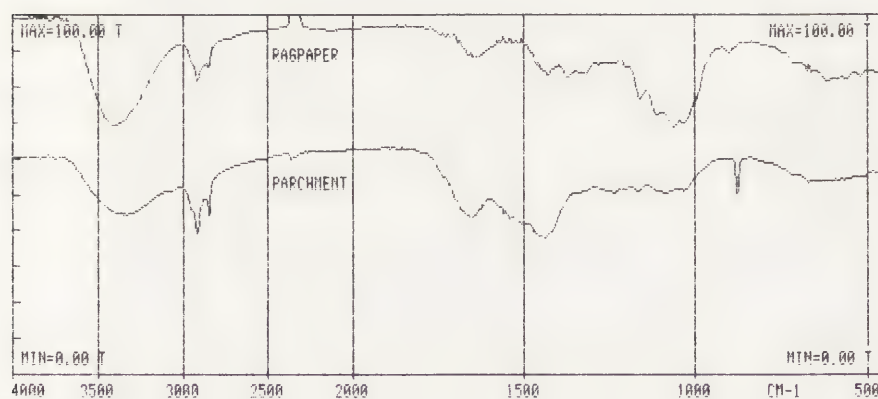


Fig. 2
Reference spectra of parchment and ragpaper.

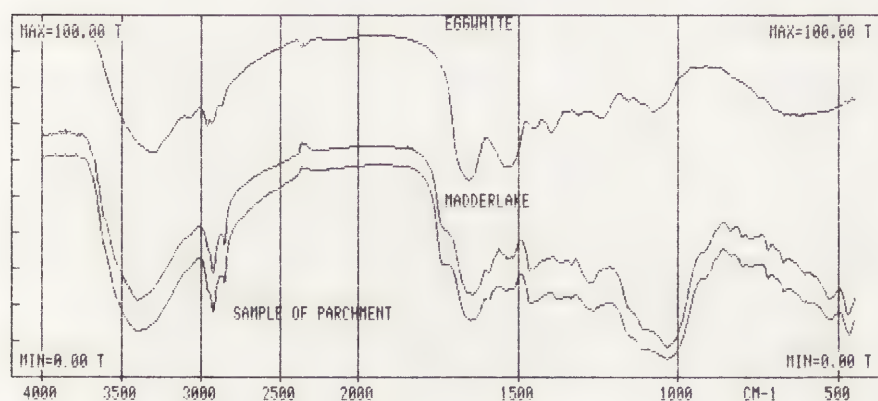


Fig. 3.
Comparison of the spectra of a sample taken from the test material,
madder lake and parchment and reference spectra of the binding
medium eggwhite and madder lake.

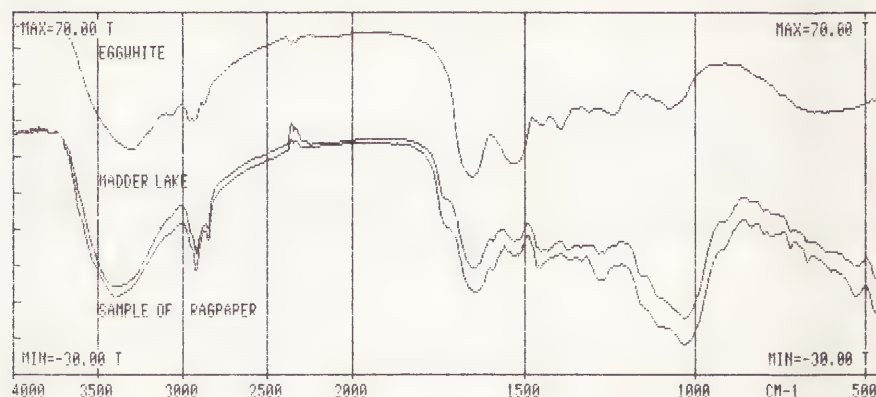


Fig. 4.

As fig. 3, sample taken from the test material madder lake and ragpaper.

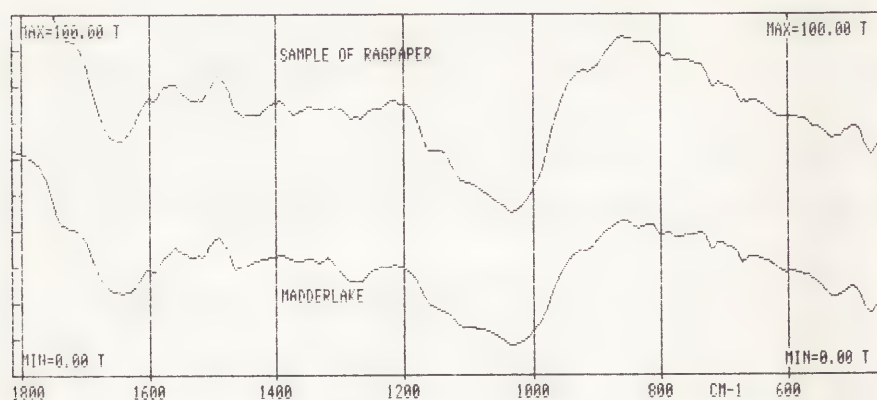


Fig. 5.

Spectra of a sample of madder lake on paper and the reference madder lake. The spectra are "zoomed" in the important part of the spectra (1800 - 600 cm^{-1}).

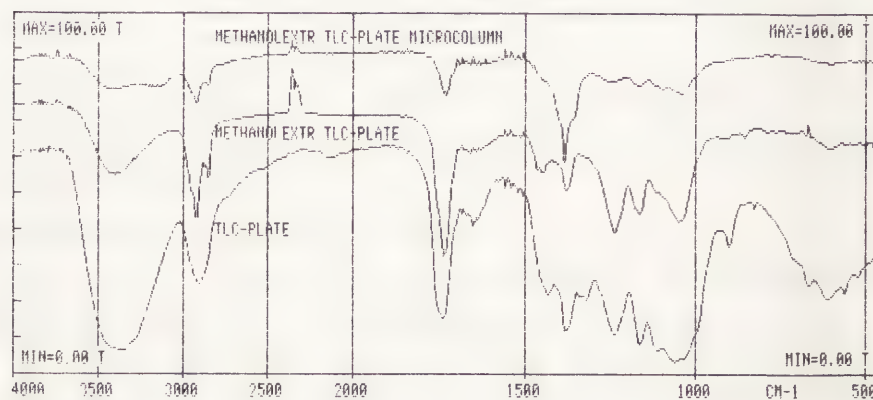


Fig. 6

Spectra obtained by the methanol extract of the TLC plate, the use of the microcolumn and the reference of the TLC plate.

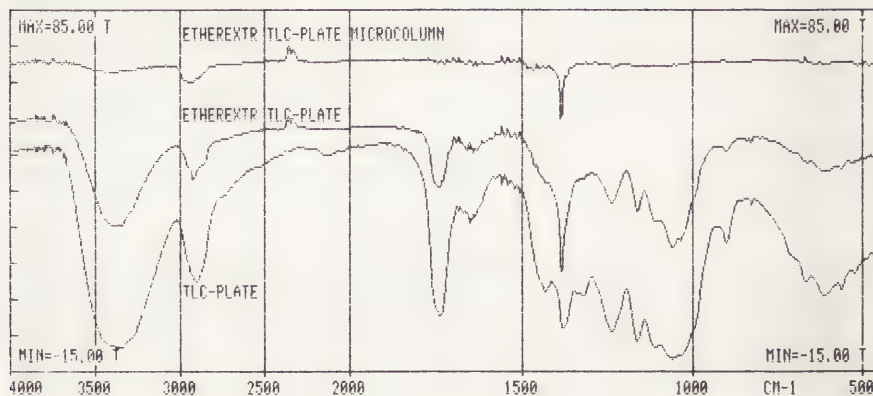


Fig. 7. As fig. 6, extract with ether.

development

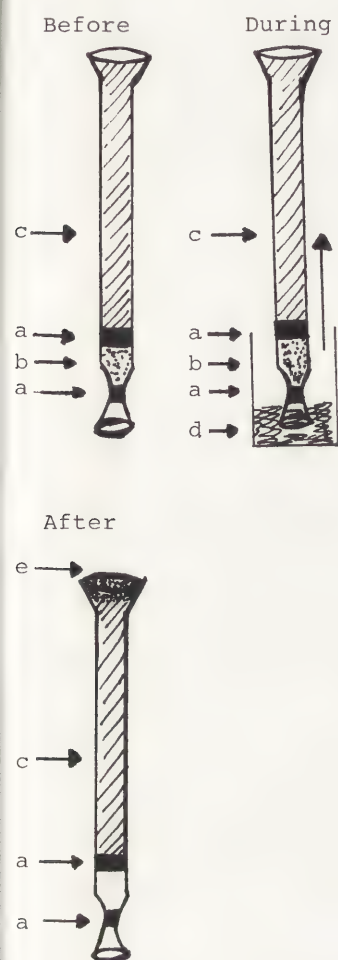


Fig. 10 micro extraction column

- = quartz wool
- = TLC plate + spot (sample)
- = pulverized potassiumbromide
- = methanol or ether
- = extracted sample in potassiumbromide

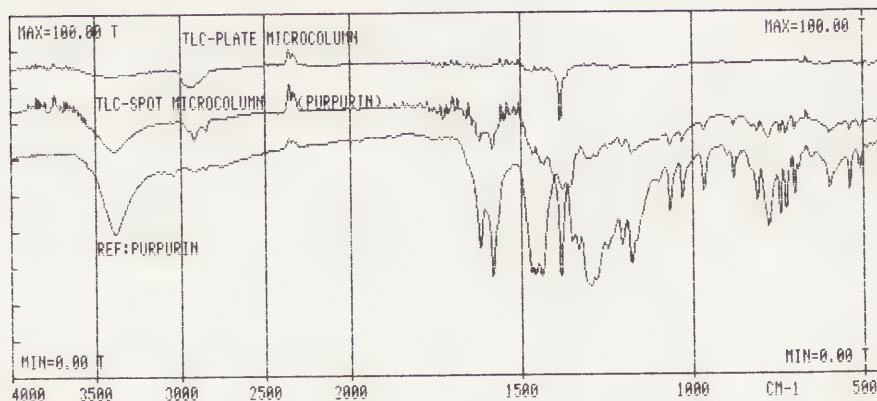


Fig. 8.

Comparison of the spectra of purpurin scraped from the TLC plate, extracted with ether through the microcolumn and the reference purpurin and TLC plate.

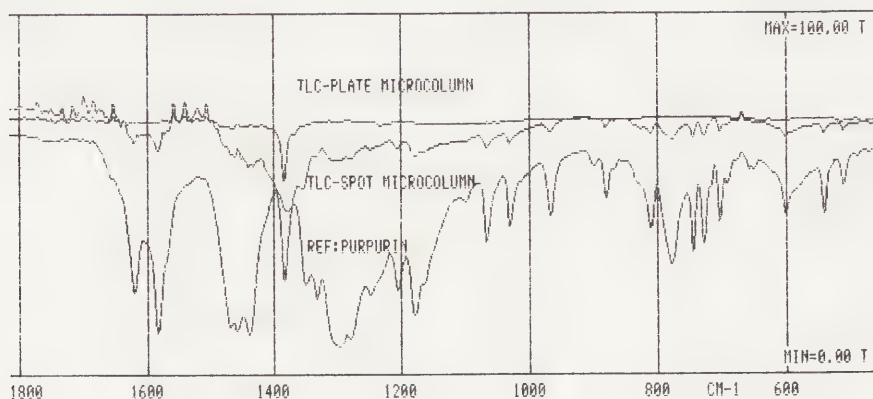


Fig. 9.

As fig. 8, spectra are "zoomed" in the area 1800 - 600 cm^{-1} .

NOTES

1. L. Masschelein-Kleiner, Microanalysis of hydroxy-quinones in red lakes, *Microchemica Acta*, 71 (1967), 1080-1085.
2. W.G.Th. Roelofs and J.H. Hofenk de Graaff, On the Occurrence of Red Dyestuffs from 1450-1600, *Proceedings of the ICOM Committee for Conservation*, Madrid, 1972.
3. J. Wouters, High Performance Liquid Chromatography of anthraquinones: Analysis of plant and insect extracts and dyed textiles. *Studies in conservation*, 30 (1985), 119-128.
4. S.M. Edelstein, D.H. Abrahams, A new method for the analysis of ancient dyed textiles; *American Dyestuff Reporter* 6, (1964), 19-25.
5. E.E. Ploss, *Ein Buch von alten Farben*, Berlin, 1962.
6. W.L.J. de Nie, *De Ontwikkeling der Noordnederlandsche Textielververij van de veertiende tot de achttiende eeuw*, Leiden, 1937.
7. P. Weigle, *Ancient Dyes for modern weavers*, New York, 1974.
8. M.P. Merrifield, *Original Treatises on the Art of Painting*, Vol II p. 432, New York, 1967.
9. T. Hirschfeld, FTIR Now and in the future, *European Spectroscopy News*, 51 (1983) 13-18.
10. D. Dekker, apparatus for the isolation of microgram amounts of compounds from thinlayers by elution and direct Millipore filtration, *J. Chromatogr.* 168 (1979) 508-511.
11. J.V. Simonian, Determination of copper in textiles by atomic absorption spectrophotometry, *American Dyestuff Reporter*, nr. 12, 1968, p. 21-24.
12. R.J. Koestler; R. Sheryll; N. Indictor, Identification of dyeing mordants and related substances on textile fibres: a preliminary study using energy dispersive x-ray spectrometry.
13. A.A. Bouman; A.J. Platenkamp; F.D. Posma, Determination of aluminum in human tissues by flameless atomic absorption spectrophotometry and comparison of reference values. *Ann. Clin. Biochem.* 23, 97, 1985.



SUMMARY

The purpose of this study is to determine what happens to fibers and pigments during various phases of treatment that is not readily visible to the naked eye or through routine magnification.

Our research project was divided into four treatment categories. The present findings are the results of four experimentations with dry cleaning treatment methods.

We selected twelve media and techniques on different types of paper of varying degrees of sizing and ten dry cleaning devices. An M-210 Carl Zeiss (Jena) microscope was used.

Results indicate that during dry cleaning procedures on small surfaces changes had occurred to fibers and pigments. In most cases, these hypothetical changes became evident only after examining the area treated under magnification. It also became necessary to examine the device itself under magnification for residual fibers and pigments. In a few cases, however, visually noted alterations could not be confirmed by magnification.

The fact that we noticed minute alterations on small areas means that the changes occurring to fibers and pigments during actual treatment will alter the overall appearance of the object.

MICROSCOPIC EXAMINATION OF WORKS OF ART ON PAPER DURING TREATMENT, IN ORDER TO DETERMINE THE EFFECTS OF TREATMENT METHODS ON FIBERS AND PIGMENTS - A joint American-Romanian Research Project

Ingrid Rose, Yvonne Efremov and Mihai Lupu

INTRODUCTION

The impetus for this project was given during treatment of a watercolor on a suction table. While the brown, acidic stains had been removed, some pigment, despite blockage, had migrated to the blotter.

This development opened a Pandora's box of questions about the effects of various treatment procedures on fibers and pigments. There had been occasions when I was struck by a vague, imperceptible change in the overall appearance of a work of art on paper. I also remember an occasion when the owner remarked on the different appearance of a print after treatment. Is it possible that fibers and pigments are affected by conservation treatment methods to a greater extent than we realize or have been able to discern?

Such questions may have occurred to conservators and curators of works of art on paper elsewhere. They had arisen at the Department of Prints and Drawings of the Art Museum of the Socialist Republic of Romania in Bucharest.

This matter raised the problem of the limits of human vision in conservation, and what can be done to have more control over the degree of interference likely to take place during treatment. To the naked eye or through the magnifying glass careful, sensitive treatment methods will not necessarily reveal changes. The idea to examine each treatment procedure under microscope gradually took shape.

We divided the project into four treatment phases: dry cleaning, aqueous, chemical, drying and flattening. We selected twelve works of art on paper in different media and ten dry cleaning devices which we grouped into three categories.

MEDIA TESTED

We examined the following works of art on paper: watercolor, tempera, sanguine crayon, pastel, charcoal, graphite, iron gall ink, and tusche drawings, lithograph (à la manière noire), lithograph, etching, drypoint.

Eight of the media were student works of the 1950's by co-author Yvonne Efremov. The tempera and sanguine crayon drawing were by unidentified art students, the iron gall ink drawing, probably done in the 1930's, by an anonymous artist, and the etching was a New Year's greeting, dated 1932, by Anton Kaindl. The paper ranged from strong wove to woodpulp of varying degrees of sizing.

DRY CLEANING DEVICES TESTED

We tested the following devices on the twelve works of art on paper for fiber disturbance and pigment abrasion, using both wiping and tapping movements, as appropriate:

I) Feathers, cotton, Japanese brush; II) Bread crumbs, Opaline powder, and III) Absorene paste, blue and white kneadable gums, Staedtler plastic and Laeuffer SW 210 erasers.

Regarding the selection of the above dry cleaning devices, we were guided by our own priorities and the availability of materials. The mechanical aspects of dry cleaning already in themselves represent elements of danger to the object and certainly constitute interference with its surface structure. Through microscopic examination, we wanted to find the degrees of interference, in order to determine which procedures and which devices might be the least harmful.

We documented our findings in twelve tables with detailed footnotes which were combined into a master table (Table I). In addition, we tested the ten devices for their elasticity, residues left on paper, and their cleaning potential, using wiping and tapping movements on a watercolor fragment of 1954 by co-author Efremov (Table II). The paper was heavy wove, medium sized, the surface and verso covered with dust and grime.

We grouped the dry cleaning devices into three categories:

I) Feathers, cotton and Japanese brush for the removal of loose surface dust; II) Bread crumbs and Opaline powder for the removal

of more resistant surface impurities, and III) Alsorene paste, blue and white kneadable gums, and two soft erasers for the removal of dust and grime embedded in the fiber structure.

We included feathers because of their use in Japanese conservation techniques. Incidentally, Japanese turkey feathers since 1984 are being used successfully at the Paper Conservation Laboratory of the Art Museum in Bucharest.

We did not include scalpels, abrasive or hard erasers, sandpaper, glass fiber and related devices because, à priori, they will cause visible alterations to the paper surface and thus fall outside the scope of our investigation.

TABLE I EFFECTS OF TREATMENT ON FIBERS AND PIGMENTS

FIBER DISTURBANCE	WATERCOLOR	TEMPERA	SANGUINE & PENCIL	PASTEL	CHARCOAL	GRAPHITE	PEN & INK	TUSCHE	LITHOGRAPH PLAN. INK	LITHOGRAPH	ETCHING	DRYPOINT
FEATHER	—	—	—	—	—	—	—	—	—	—	—	—
COTTON	—	—	—	—	—	—	—	—	—	—	—	■
BRUSH	—	—	—	—	—	—	—	—	—	—	—	—
BREAD CRUMBS	—	—	—	—	—	—	—	—	—	—	—	—
OPALINE	—	—	—	—	—	—	—	—	—	—	—	—
ABSORENE	■—	—	—	—	—	—	—	—	—	—	—	—
BLUE GUM	■ ■	—	—	—	—	—	—	—	■	—	■	—
WHITE GUM	■ ■	—	—	—	—	—	■—	—	■	—	■ ■	—
STAEDTLER	—	—	—	—	—	—	■—	—	—	—	■—	—
LAEUFER	■—	—	—	—	—	—	■	—	—	—	■—	—
PIGMENT ABRASION												
FEATHER	□	■	□—	■ ■	■	□	□	—	□	—	—	—
COTTON	□	■	□—	□	□	■	—	—	—	—	—	—
BRUSH	□	□	□—	□	□	□	—	—	—	—	—	—
BREAD CRUMBS	□	□	—	■	■	■	—	—	—	—	—	—
OPALINE	□	□	—	■	□	□	—	□	—	—	—	□
ABSORENE	■	□	□ ■	■ ■	■ ■	■ ■	—	—	□ □	—	—	—
BLUE GUM	■	■ □	□ □	■ ■	■	■	— □	— □	□ □	—	—	□—
WHITE GUM	■	■ ■	■ ■	■ ■	■ ■	■	■ ■	□	□ □	—	■ □	□ □
STAEDTLER	■ ■	■ ■	■ ■	■	■	■	□—	□—	—	—	■ □	■—
LAEUFER	■	■	■ ■	■ ■	■	■	■	■—	—	—	□—	■—

■ = MUCH □ = MEDIUM □ = SOME — = NONE

By Mihai Lupu

Two rows in a square: Left block = Wiping Motion
Right block = Tapping Motion

EXPERIMENTS AND RESULTS

Surface Disturbance

Our hypotheses of surface disturbances eluded early clearcut, concrete evidence. When examined under increased magnification, the test area of one cm^2 , treated with the dry cleaning devices in categories I and II seemed little or not at all disturbed. The more potent devices of category III caused surface alterations of varying degrees, depending upon the quality of the paper surface, the degree of sizing, and the treatment method.

Pigment Abrasion

Experimenting with the dry cleaning devices of categories I and II, we could not determine with precision, even with maximum magnification of 100 x, the amount of pigment abrasion that might have occurred on the test area of one cm^2 . The devices of category III were not much more conclusive, except, as was to be expected, on the unfixed pastel and charcoal drawings of the 1950's by co-author Efremov. Looking at the dust and dirt particles adhering to the devices or mixed in with the cleaning residues, we hypothesized that they might contain more matter than only extraneous surface dirt particles.

During an experiment on a tempera drawing, we noticed that cotton filaments had lifted some pigment particles. Since inked or pigmented fibers are stiffer than non-pigmented fibers, the dry cleaning movement with cotton could risk bending or breaking them, ultimately altering the general image and overall surface texture of the object.

During our experimentation with the lithograph à la maniere noire, a noteworthy incident occurred. Wiping and tapping motions with Absorene and blue and white kneadable gums on a one cm^2 test spot of the pigmented image resulted not so much in pigment abrasion as in a lifting and realignment of a pigmented fiber, revealing the white paper fibers (Figure 1). In lithography à la maniere noire, the image is created out of the inked lithographic stone by scraping. In this case, the tusche may have been more diluted with distilled water than customary. Furthermore, the carrier was a poor quality wove paper, weakly sized. These factors may have contributed toward the ink's adhering rather weakly to the paper surface. Notwithstanding these explanations, the fact that a fiber was lifted was cause for concern. It does not take much imagination to understand that a lifting and realignment of pigmented fibers, in proportion to the surface treated, will no doubt result in a change of appearance.

It became soon apparent during our experimentations that it was not enough to examine under microscope only the works of art on paper, but that the dry cleaning devices, residues on same, as well as residues left on paper, merited microscopic examination as well. Examination of the dry cleaning devices helped us understand how the structure of a given device can affect fibers and pigments. It showed us the characteristics of the devices tested and enabled us to observe the interaction of a device with the paper surface and the resulting degree of fiber disturbance and pigment abrasion.

I. Feathers, Cotton, Japanese Brush

The examination of cotton, a Japanese brush and feathers, at a magnification of 25 x, showed us the following regarding their cleaning action on fibers and pigments:

Cotton filaments tended to get caught by the burr of the intaglio lines as well as by rough pigmented surfaces. If a device as inoffensive as cotton gets caught, we should be concerned that dry cleaning with cotton may break off some burr or disturb pigments, and thus distort the image of the object (Figure 2).

When we examined the Japanese brush (Figure 3), we noticed that the fine natural hair dragged surface dust across the object. This could lead to abrasion of pigments and disturbance of fibers. (We were surprised to note that the surface fibers remained undisturbed when brushing against the grain, but that they became unsettled when brushing with the grain. This phenomenon has to be looked into further.)

Regarding our examinations of Romanian pigeon and Japanese turkey feathers, we should like to remind readers of the use of feather dusters in the past. Even though the analogy of a feather (nature's gift to conservation?) with contemporary highly

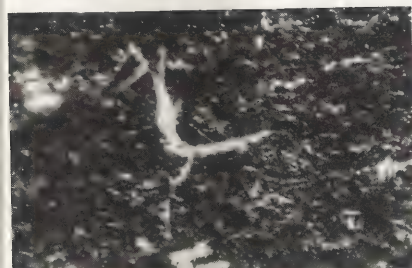


Figure 1 Lifting and re-alignment of a pigmented fiber. Magnification 20 x.



Figure 2 Cotton filaments. Magnification 30 x.



Figure 3 Japanese brush. Magnification 30 x.

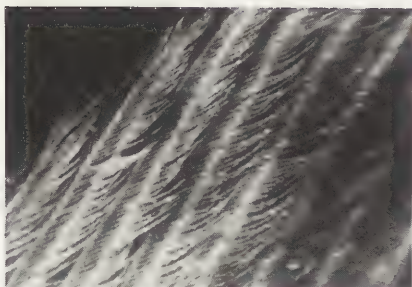


Figure 4 Japanese turkey feather; outside vane. Magnification 30 x.

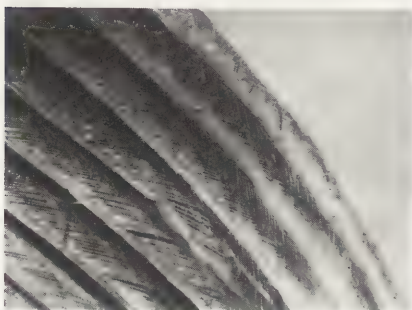


Figure 5 Japanese turkey feather; inside vane. Magnification 30 x.

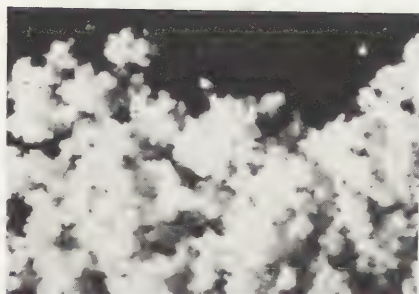


Figure 6 Opaline powder. Magnification 30 x.

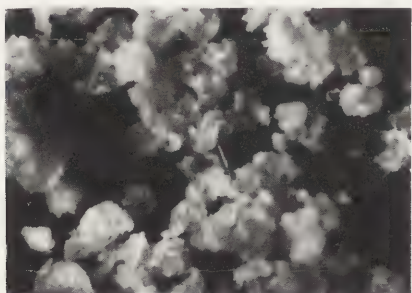


Figure 7 Bread crumbs. Magnification 30 x.

advanced equipment and treatment methods may evoke smiles, we think that we may have found an explanation of why feathers were used in the past, why they are an important dry cleaning device in Japan today, and why they lend themselves to gentle and effective removal of surface particles from Western papers.

Magnification of a Japanese turkey feather at 25 x already showed an impressive physical structure on either side of the vane. On the outside vane, overlapping barbules and barbels form a network of minute hooks between the barbs (Figure 4), while the inside vane is composed of grooves (Figure 5). Although the outside vane feels and looks smooth, its surface in reality is rather rough, and cleaning action could be abrasive. Moreover, more dust particles tended to get stuck to the edge of the outside vane, thus increasing the risk of fiber disturbance and pigment abrasion. In comparison, the inside vane during cleaning movements, by sweeping from right to left, collected more dust particles on the vane, as they moved upward inside and alongside the grooves, away from the edge. The fact that dust and surface particles are held in place, as if by static electricity, endows the feather with unique dry cleaning possibilities. Held in place, fewer dust and loose particles will be dragged across fibers and pigments, lessening the risk of fiber disturbance and pigment abrasion.

The use of cotton and brushes presents a built-in problem, because dust and other particles are dragged across the paper surface, whereas cleaning motions with the inside vane of feathers reduce this risk.

II. Bread Crumbs and Opaline Powder

Bread crumbs are still in use in Romania for cleaning works of art on paper. We included one-day old wheat bread from a bakery in Bucharest in our experimentations and compared them with Opaline powder. Apart from microbiological concerns which are especially relevant in humid climates, bread must be aged just right to be used effectively. It may not be too dry nor too moist. It must be used at a relative humidity that keeps it from drying and becoming hard and crusty or from turning moist and sticky.

In our experimentation with an etching of a 1932 New Year's greeting card by Anton Kaindl, we detected no surface disturbance or pigment abrasion on the paper. However, we noticed visually that the tone of the bread crumbs had changed after application and that they reflected the purple color of the etching ink. Magnification of up to 100 x was not sufficient to reveal a single pigment hidden inside the crumbs. Comparison with a batch of unused crumbs confirmed visually that a transfer of pigment had to have taken place. In this particular case, we had to rely on our eyes because microscopic examination of both the tested area and the bread crumbs at a maximum available magnification of 100 x yielded no clues.

The same experiment conducted with Opaline powder also revealed a visual change in shading of the used powder particles. Pigment particles were detected inside the used powder at a magnification of 100 x.

We subsequently carried out a special experiment on a scale of watercolor pigments prepared a dozen years ago by co-author Efremov. Visually, bread crumbs and Opaline powder had both changed in tone after application. Upon magnification of both dry cleaning devices, we now noticed isolated pigment particles nestled inside bread crumb clusters, while we detected no pigment particles whatsoever in the Opaline powder. Although the test area of ca. one cm² looked unchanged visually, successively increased magnification revealed abrasion of the pigmented surface at a magnification of 100 x.

If this abraded, experimental area were multiplied by the actual size of the treated object, it is clear that pigment loss would be multiplied proportionately. The density of the pigments would be broken up and the pigment layers thinned, thus affecting the brilliance of the colors.

The physical characteristics of bread crumbs and Opaline powder inhibit dragging action. Under magnification, Opaline powder particles (Figure 6) are harder than properly aged bread crumbs which, although uneven in their physical components (Figure 7), are a little more elastic than Opaline powder, thus ensuring somewhat better control during treatment.

Both devices require mechanical removal of their dust-covered particles from the surface of the object. Here the danger to fibers and pigments of dragging is apparent.

Since both bread crumbs and Opaline powder could leave even after careful cleaning minute residual particles on the paper surface which may embed themselves in the fibers and pigments, depending on the surface structure and technique, the use of these devices should be gauged with care.

Given our findings regarding the use of Japanese turkey feathers for loose dust removal, it may be recommendable to use turkey feathers in addition to or in lieu of traditional brushes and cotton for the lifting of residual eraser flakes, crumbs, powder, and other loose particles.

TABLE II SURVEY OF DRY CLEANING DEVICES ON WATERCOLOR PAPER

DEVICE	ELASTICITY	RESIDUES LEFT ON PAPER*		CLEANING POTENTIAL	
		WIPE	TAP	WIPE	TAP
FEATHER	N/A	No	N/A	C+	N/A
COTTON	N/A	Yes	N/A	C+	N/A
JAPANESE BRUSH	N/A	No	N/A	C+	N/A
BREAD CRUMBS	B+	No	N/A	A	N/A
OPALINE POWDER	B	No	N/A	A	N/A
ABSORENE PASTE	A	Yes	No	A	N/A
BLUE KNEADABLE GUM	A	Yes	No	A	B+
WHITE KNEADABLE GUM	A	Yes	No	A	B+
STAEDTLER PLASTIC ERASER	B	Yes	No	A	B+
LAEUFER SW 210 ERASER	B+	No	No	A	B

*after brushing

A = MUCH B = MEDIUM C = SOME D = NONE N/A = NOT APPLICABLE

III. Absorene Paste, Kneadable Gums, Soft Erasers

The dry cleaning devices in this category are by virtue of their nature more potent and effective. At the same time, they are more dangerous to fibers and pigments (Figure 8).

On the whole, Absorene paste proved to be an effective, relatively benign device. Nevertheless, prudence is called for when using it. We found that the surface of normally sized, smooth wove paper felt sticky after treatment with Absorene. For example, when tapping on a test spot of the 30-year old tusche drawing on well-sized paper with Absorene, microscopic examination of the Absorene particles revealed that pigment particles had been lifted and were visible in the crevices of the magnified Absorene. (Absorene particles must be removed from the paper surface immediately, or else they will harden and become encrusted in the fibers and pigments.)

We used wiping and tapping motions without noticeable changes to well-sized paper surfaces. The fibers of poorly sized papers were disturbed. A third motion, namely rolling Absorene paste, or kneadable gums, across the paper surface may be less drastic and harsh on weak surfaces.

Experimentations with two kinds of kneadable gums and two types of soft erasers confirmed them to be, on the whole, effective devices for the removal of surface grime and soot. Of the two kneadable gums, the white one, less sticky to the touch and to handling than the blue one, tended to leave particles behind on three of the twelve works of art on paper tested. All three were medium to heavy sized.

We were stunned to discover that an eraser known to be soft and relatively harmless, Laeuffer SW 210, probably made of rubber, had abraded both fibers and pigments of a drypoint. The abrasion was vaguely visible to the naked eye. Magnification confirmed a shifting of fibers and a thinning of the pigmented surface. Also visible to the naked eye were traces of discoloration on the eraser which could be interpreted as surface dust that had been

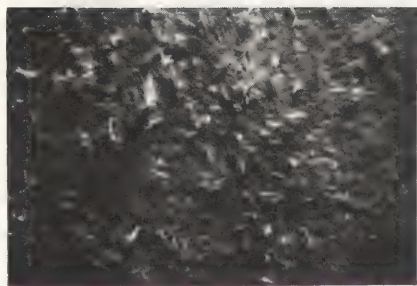


Figure 8 Surface disturbance caused by blue gum. Magnification 12 x.

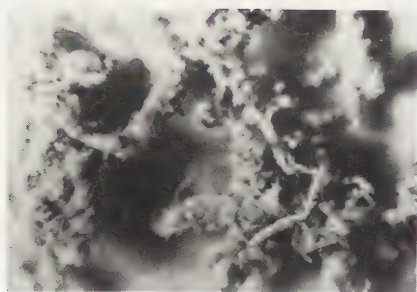


Figure 9 Laeuffer SW 210 eraser residues with dust, fibers and pigments. Magnification 20 x.

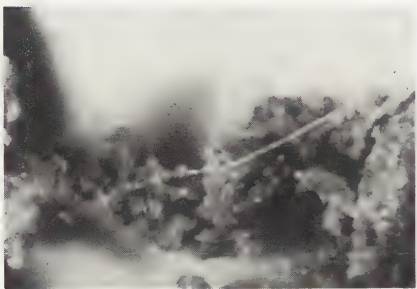


Figure 10 Staedtler Plastic eraser residues with dust, fibers and pigments. Magnification 20 x.

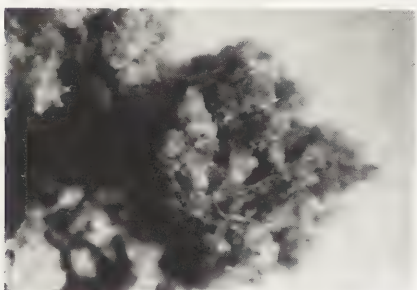


Figure 11 Boston eraser cleaner residues with dust, fibers and pigments. Magnification 20 x.

removed from the object. Under magnification, however, the discoloration turned out to be a mixture of dirt plus fibers and pigments. We then examined the eraser crumbs of this and other erasers and recognized fiber and pigment particles, indicating even further loss of fibers and pigments (Figures 9, 10 and 11). We were even more astonished by the microscopic make-up of the Laeuffer SW 210 eraser. At a magnification of 100 x, the ingredients of this eraser looked like an agglomerate of sand particles embedded in an elastic mass of caoutchouc. This soft and pliable eraser used in mechanical dry cleaning, upon magnification revealed unexpected, abrasive characteristics. Microscopic examination of art and plastic erasers ("Boston eraser cleaner" and Eberhard Faber "Star gum cleaner" No. 4833 as well as Staedtler Mars-Plastic No. 52650) revealed no pebbles within the elastic mass.

Certainly, we shall pay more attention to the properties of soft erasers in future dry cleaning treatments.

Upon experimentation with the two kneadable gums and erasers on an iron gall ink drawing of 1931, we found during magnification traces of pigments and fibers on the devices. Yet, no fibers appeared to have been disturbed in the uninked areas. We hypothesized that the acidity of the ink may have weakened the fibers, thus aiding the separation from the paper surface. Here we experienced yet another reaction of fibers to mechanical dry cleaning devices.

While the aforementioned changes to fibers and pigments had occurred on a test surface of ca. one cm², with few or no clear surface alterations visible to the naked eye or through magnification it was only when we visually inspected the mechanical dry cleaning devices and noticed what could be interpreted as dust specks that we became suspicious and decided to examine them further. With increasing magnification, the dust specks turned into a mixture of just those plus fibers and pigments, confirming our hypothesis that the paper surface had been not only disturbed and abraded, but that fibers and pigments had been lost irrevocably. These losses will result in a change of appearance and affect the integrity of the work of art on paper and violate the artist's intent.

CONCLUSION

The importance of the first findings of our experimentations lies in the realization that although visually nothing untoward may be taking place during conservation treatment, microscopic examination of both the objects and dry cleaning devices will reveal that the effects of treatment may indeed have altered the surface of a work on paper by disturbing its fibers and abrading its pigments.

We realized that it was not enough to examine the object alone, but that each dry cleaning device had to be examined under microscope as well. Understanding the physical properties and mechanics of dry cleaning devices clarified the interrelationship between them and their potential effects on fibers and pigments. As a consequence, we were able to compare the actual effects of treatment which in turn made us more judicious in selecting the appropriate dry cleaning device.

As a result of our work, we think that the microscope should be an integral part of conservation treatment. Large institutions and laboratories are equipped with advanced microscopic equipment. Although small organizations and individual conservators may find it costly to acquire a microscope, its acquisition should be a good investment in the long run because it will help them become more knowledgeable and increase their acuity and dexterity.

Working at every stage of our experimentations with a microscope was a continuous consciousness-raising experience, during which we developed an increased respect for the integrity of the object.

We became aware of our limitations during the study and also of our power over the object, which can be used positively or destructively. These are preoccupying issues for our profession. They have to do with the ethics of conservation and also with aspects of preventive conservation. If we acknowledge that any degree of treatment, however necessary and benign, constitutes interference with the integrity of the object, we consequently have to accept that less intervention may be the better treatment. Yet this argument does not help conservators when faced with deteriorating objects in need of treatment which, if left unaided, would disintegrate and ultimately be lost. Treatment is and will be necessary. It is the quality of treatment that matters.

We hope that with increased awareness and sensitivity the conservation community will understand how even the most inoffensive

treatment method may alter and cause irreversible harm to an object. We further hope that our findings and ideas will inspire conservation educators in training future conservators.

Although we come from backgrounds of different education and training, our collaboration developed into a true meeting of the minds on behalf of the goals of conservation.

ACKNOWLEDGMENTS

We are deeply grateful to Mrs. Suzana Gădea, Minister of Culture of the S.R. of Romania, and Dr. Alexandru Cebuc, Director of the Art Museum of the S.R. of Romania, for their interest and support.

REFERENCES

- 1 AIC Code of Ethics and Standards of Practice, AIC Directory 1986-87. The American Institute for Conservation of Historic and Artistic Works, Washington, DC.
- 2 ALTHOEFER, Heinz. Historische und ethische Prinzipien der Restaurierung. Third International Restorer Seminar on Problems of Completion, Ethics and Scientific (sic) Investigation in Restoration, Veszprém, Hungary, 1981. Pub. Institute of Conservation and Methodology of Museums, Budapest, 1982.
- 3 BALLESTREM, Agnes. Darf der Restaurator restaurieren? Fourth International Restorer Seminar on Restorer's-Museologist's-Scientist's (sic) Common Responsibility in the Protection of Museum Objects, Veszprém, Hungary, 1983. Pub. National Centre of Museums, Budapest, 1984.
- 4 BANKS, Paul. "Paper Cleaning," *Restaurator* I (1969) 52-56.
- 5 BARTON, G. and WEIK, S. "Ultrasonic cleaning of ethnographic featherwork in aqueous solutions," *Studies in Conservation* 31 (1986) 125-132.
- 6 GRIFFITHS, A. Prints and Printmaking. An Introduction to the history and techniques. Pub. British Museums Publications Limited, 1980.
- 7 H. HOFENK DE GRAAF, J. The Cleaning of Paper and Its Influence on the Surface. Veszprém Postprints, 1981.
- 8 JEDRZEJEWSKA, H. The Concept of Reversibility as an Ethical Problem in Conservation. Ibid.
- 9 JEDRZEJEWSKA, H. Psychological Factors in Conservation and Museology - A Preliminary Study. Veszprém Postprints, 1983.
- 10 MAYER, R. Gedruckte Kunst. Wesen, Wirken, Wandel. VEB Verlag der Kunst Dresden 1984.
- 11 ROBISON, A. Paper in Prints. National Gallery of Art. Washington, DC 1972 (?).
- 12 MORGÓS, A. The Protection of Art Objects and the Chemist's Ethical Approach. Veszprém Postprints, 1981.
- 13 VIANA, M.F. L'Etat de Surface originale et la restauration. Veszprém Postprints, 1981.
- 14 WAECHTER, O. Restaurierung und Erhaltung von Büchern, Archivalien und Graphiken. Hermann Boehlaus Nachf. Wien, 1982.
- 15 WAECHTER, W. Buchrestaurierung. Das Grundwissen des Buch- und Papierrestaurators, VEB Fachbuchverlag Leipzig, 1981.
- 16 WETERING, E. van de. Die Oberflaeche historischer Gegenstaende im Licht der Zeit. Veszprém Postprints, 1981.

INGRID ROSE is a paper conservator in Washington, DC. Currently she lives in Bucharest, Romania, where her husband works for the U.S. Government.

YVONNE EFREMOV is Chief Paper Conservator at the Art Museum of the S.R. of Romania in Bucharest.

MIHAI LUPU is Conservation Chemist at the Art Museum of the S.R. of Romania in Bucharest.

PHOTO CREDITS

CORNELIA ȘOANCA and IOANA ZAHARIA, Photographic Laboratory of the Art Museum of the S.R. of Romania in Bucharest.

SUMMARY

The usefulness of sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) could be shown in order to demonstrate various stages of structural damage in selected parchment samples. As a consequence experiments were carried out to simulate the action of copper pigments on parchment structure in the course of ageing under controlled environment.

Copper (II) acetate as well as copper (II) sulfate were applied. It could be shown that - most probably as the primary step of degradation-conformational change, i.e. unfolding of the protein chains, is induced by the action of copper(II)-ions. Generally, this change results in higher electrophoretic mobilities of all components observed. It is concluded that much longer ageing would be required to bring about structural damage similar to that of samples from original objects of art.

ELECTROPHORETIC INVESTIGATIONS ON PARCHMENT DECAY

H.Stachelberger¹⁾, A.Haberditzl¹⁾, G.Banik²⁾, F.Bauer³⁾, F.Mairinger⁴⁾

- 1) Institut f. Angewandte Botanik, Technische Mikroskopie und Organische Rohstofflehre d. Technischen Universität, Getreidemarkt 9, A-1060 Wien, Österreich
- 2) Institut f. Restaurierung, Österreichische Nationalbibliothek Josefsplatz 1, A-1015 Wien
- 3) Institut f. Fleischhygiene, Fleischtechnologie u. Lebensmittelkunde, Tierärztliche Universität, Linke Bahngasse 11, A-1030 Wien, Österreich
- 4) Institut f. Farbenlehre u. Farbenchemie, Akademie der Bildenden Künste, Schillerplatz 3, A-1010 Wien, Österreich

Introduction

In the course of investigations concerning the elucidation of the mechanisms of the degrading action of copper-pigments as well as iron-containing inks on parchment from medieval and recent manuscripts and from works of graphic art, respectively, experiments were undertaken to demonstrate changes of the collagen proteins in damaged as well as undamaged parchment samples by means of sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE).

On the basis of scanning electron microscopic studies the heavy decay of fibrillar parchment structure as a consequence of the action of transition metal ion-containing inks could be clearly shown (1). Furthermore, in aged and highly damaged parchment samples a decrease of disulfide and sulfhydryl groups paralleled by an increase of total sulfur could be observed, thus indicating the involvement of certain functional groups of collagen in the various processes taking place under unfavorable environmental conditions (2).

These findings led us to the assumption that the degree of structural damage in parchments could be well associated with changes in the molecular weight distribution of collagen proteins as revealed by the application of SDS-PAGE.

Experimental

10 mg of finely cut up parchment were suspended in 2 ml 0.125M tris-borate-buffer (pH 8.9) containing 1% sodium dodecyl sulfate (SDS), 1% 2-mercaptoethanol and urea (4M). Right before carrying out the electrophoretic separation suspensions were kept at 80°C for 5 min. 20 µl of the suspensions were run at 260 Volts for 60 min. in 5% polyacrylamide gels containing 1% SDS and urea (4M) (3). Running distance of samples was 60 mm. The size of the gel blocks was 100x100x3 mm.

Simulation experiments were done by either spreading suspensions of powdered copper acetate in animal glue on fresh parchment samples or soaking parchment samples with 0.1% CuSO₄-solutions and keeping the dried samples at 50°C and 80% relative humidity for different periods of time.

Results and Discussion

Under the experimental conditions described above, selected samples of parchment were examined (4) and in the case of fresh calfskin parchment it was possible to demonstrate the distribution of collagens according to HAYASHI & NAGAI (5). In a mixture of collagen type I and III the α₁-, β- and γ-components could be clearly demonstrated. Due to the presence of urea the separation of α₁(I)- and α₁(III)-components was also possible. Three stages of degradation were defined on the basis of electropherograms from different parchment samples (Fig. 1). In samples of obviously well preserved and flexible calfskin parchment with ink writing dated from the 18th century the α-chains could be clearly seen whereas the β-chains were only very faintly stained and γ-chains were not detectable any more thus indicating a marked decrease in the degree of cross-linking. This was designated by us as the first stage in the degradation of parchment structure. Samples of a stiff and darkened binding from calfskin parchment showed distinct bands only in the α-region marking the second stage of

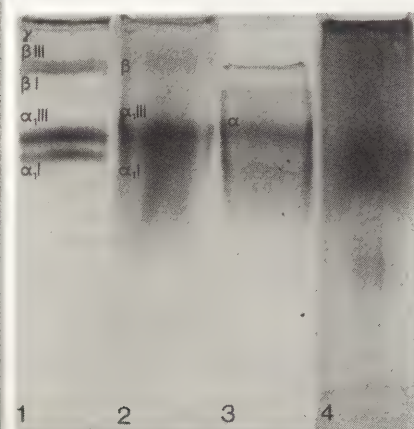


Fig.1: Electrophoretic patterns of various samples of calfskin parchment;
(1) undamaged
(2) slightly damaged
(3) moderately damaged
(4) extremely damaged

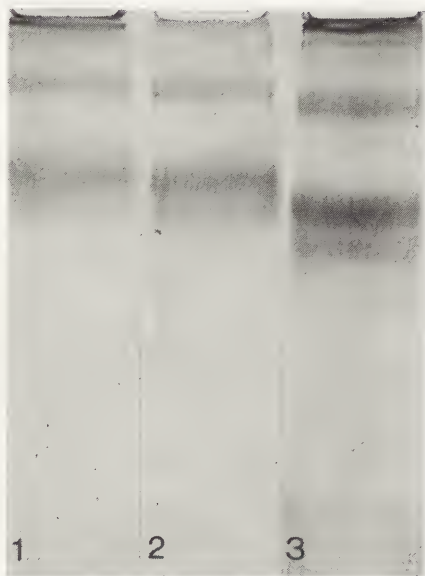


Fig.2: Migration distances of collagen proteins in
(1) untreated,
(2) copper acetate-, and
(3) copper sulfate-treated
samples from calfskin
parchment

parchment degradation. The third and worst stage of degradation represented by extreme brittleness of the samples is reflected electrophoretically in a complete loss of any distinct band typical for collagens. It was found either uniform staining extending into the low-molecular weight range or the occurrence of diffuse bands with lower molecular weight. Electropherograms of this kind were found in samples of a Flemish manuscript from the 15th century as well as in samples from undated antique parchment and the back of a book binding having been exposed to sunlight and dust over longer periods of time.

It seemed therefore to be of utmost interest if there was a possibility to demonstrate the action of copper containing pigments on parchment structure in the course of simulation experiments (6). On behalf of the question, samples of fresh parchment were treated with suspensions of copper acetate in animal glue as a binding medium. The dried samples were artificially aged for 56 hours at 50°C and 80% relative humidity. During this procedure the pigment happened to decompose into brownish-black, crumbly cupric oxide. The typical "Kupferfrass"-reaction between copper acetate and parchment could not be achieved this way. Furthermore, it has shown necessary to remove copper ions by shaking the samples 24 hours in 2% EDTA-solution prior to electrophoretic runs. This step became necessary because reaction of urea with the original copper pigments as well as with the resulting copper oxides leads to the formation of deep blue cupric ammine complexes in the presence of which the proteins undergo heavy decomposition regardless of other pigment-protein interactions. Electropherograms of samples treated in the forementioned way generally show all bands of intact collagen (α -, β - and γ -components). Compared to untreated parchment, however, greater migration distances of the components are found (Fig. 2). Similar results are achieved in the case of parchment samples having been soaked for 24 hours with 0.1% copper(II)-sulfate-solutions and subsequently aged for 6 days under the same conditions. The greenish discoloration occurring during the soaking process does not alter during the ageing experiments. Compared to the treatment with copper acetate much more copper(II)-ions should be available for the reaction with collagen in this case. Therefore the migration velocity of collagen components is found to be noticeably higher than after reaction with copper(II) acetate (Fig.2).

Conclusion

Considering the results of our experiments a preliminary conclusion can be drawn in that for the simulation of "Kupferfrass" soaking of parchment samples with solution of copper(II) salts should be preferred over spreading of suspensions of copper pigments. In order to achieve noticeable decay of parchment structure the duration of artificial ageing should be considerably longer than one week. The first stage concerning the interactions between copper(II)-ions and collagen is obviously represented by conformational changes of the protein molecules resulting in altered binding capacities for SDS as shown by higher electrophoretic mobilities of the collagen components. From a practical point of view these conformational changes probably going along with unfolding of certain domains within the protein molecules should be interpreted as the primary step in the degradation of protein structure leading to an increased reactivity of the molecule towards a wide spectrum of chemical compounds.

Acknowledgements

The research project "Untersuchungen der destruktiven Wirkung von grünen Kupferpigmenten auf Papier und Pergament sowie Entwicklung geeigneter konservatorischer Maßnahmen" is being supported by the Stiftung Volkswagenwerk. Collaborating institutes are the Österreichische Nationalbibliothek, Vienna, and the Staatsbibliothek Preussischer Kulturbesitz, Berlin (West). The authors thank the Stiftung Volkswagenwerk for the support which made the present work possible.

Thanks for leaving sufficient sample material are due to the Manuscript Department (Österr. Nationalbibliothek, Vienna) and Messrs. Carl Wildbrett, D-8903 Bobingen, FRG.

References

- 1) H.Stachelberger, G.Banik, M.Schreiner, F.Mairinger,
Beitrag elektronenmikroskop. Direktabb. Oberfl. 16 (1983)
p. 321-328
- 2) A.Haberditzl, H.Stachelberger, G.Banik, F.Bauer, F.Mairinger,
ICOM Committee for Conservation, Preprints to the
7th Triennial Meeting, Copenhagen, Sept.1984, Vol. II,
84.14.5 - 84.14.7
- 3) K.Khan, W.Bushuk, Cereal Chem. 54 (1977) p.588-596
- 4) A.Haberditzl, F.Bauer, H.Stachelberger, G.Banik, F.Mairinger,
Proc. 5th Meeting of the Int. Electrophoresis Society
(Electrophoresis 86), London, Sept. 9-12, 1986, p.356-358
- 5) T.Hayashi, Y.Nagai, J.Biochem. 86 (1979) p.453-459
- 6) H.Stachelberger, A.Haberditzl, F.Bauer, G.Banik, F.Mairinger,
Proc. Elektrophorese Forum 86, 6. Diskussionstagung,
TU München, 27 - 28. Oktober 1986, p. 351-355



SUMMARY

A description of the historic building, archives and work spaces and processing procedures, is followed by a discussion of various types of tracing papers, dating from 1860 to 1950, with details on treating resinous papers, removing self-adhesive tapes, penetration of non-aqueous deacidification solutions and use of heat set tissues for repair of large size tracing papers which are stored rolled.

TREATMENT OF 19TH CENTURY TRACING PAPERS FROM THE FREDERICK LAW OLMSTED COLLECTION

Janet L. Stone
Frederick Law Olmsted
National Historic Site
99 Warren Street
Brookline, MA 02146, USA

Background

Frederick Law Olmsted (1822-1903) is considered to be the father of American Landscape Architecture. His interest in parks was inspired by an 1850 visit to Birkenhead Park, a public park outside Liverpool. Here he realized that parks could serve working people as a refuge from the crowded conditions of industrialized urban life. Soon after, he and Calvert Vaux designed Central Park in New York City. In 1883 he established a firm at his home in Brookline, near Boston, Massachusetts. He worked on landscaping public parks, suburban communities, college campuses, hospitals, and private estates. He was especially interested in landscaping massive "country parks" in urban settings. His goal was to civilize the cities by creating beautiful spaces to increase "communicativeness", his term for a democratic social intermingling which leads to understanding and kindness among people. His work at Yosemite and his thoughts on preservation of natural resources were influential in the founding of the U.S. National Park Service. In 1901 his son, Frederick Law Olmsted Jr., became the first director of the Department of Landscape Architecture at Harvard University where the Olmsted influence remained strong for over half a century. The younger Olmsted also wrote the enabling legislation for the National Park Service, established in 1916. The firm was carried on by the two Olmsted sons until 1950. In all, it was responsible for some 5000 design jobs.¹

The National Park Service acquired the Olmsted property as a National Historic Site in 1980. It is a rambling frame structure on landscaped grounds. The structure includes the home and the added offices and drafting rooms of the Olmsted firm with an attached three story brick storage vault. It is one of the few National Parks to be significant principally because of its archival holdings.

The buildings and grounds of the Site are open to the public for tours three days a week. The archives are open five days a week but because the documents are stored off-site, researchers must make appointments to see specific materials in advance. Research requests often necessitate a time consuming search for materials which frequently need inventorying and treatment before they can be made available.

The plans, as stored by the firm, were rolled tightly onto wooden dowels or onto each other and were stuffed into 6"x6"x4" (15x15x12cm) wooden compartments in the unheated, unventilated vault. Floods had destroyed the paper in the lowest tiers of the lower vault and many plans suffered from mold, bacterial damage, grime and physical abuse. Since the Olmsted firm had organized their plans storage by job, tracings, blueprints, sunprints, architectural linens and large backed drawings and prints were usually rolled together. All have undulations and many are creased, crushed and torn (Figure 1). A one per cent survey of the collection suggests that there are more than 115,000 plans ranging in size from small fragments to maps as large as 1x8 meters. Possibly one fourth of the total are on tracing papers. To prepare for vault renovation, the contents of each compartment were transferred to an individual acid free tube. Over 2000 tubes were transported horizontally to temporary storage 90 miles from the Site. Our ultimate goal is to house them in flat storage in the renovated vault.

The conservator's main responsibilities are to define and assure the quality of the storage environment by establishing tube, folder, and interleaving material specifications and vault shelving design, and to work out the optimum treatment for each type of plan. The need to ready such a large number of plans as soon as possible while working in an old building with a small staff may necessitate delaying complete treatment.²

In 1984 a temporary conservation laboratory was established in three former bedrooms of the house portion of the site. The potentially useful but historically significant large drafting rooms could not be used since they are to be accurately restored to interpret the site for visitors, precluding any structural modification such as the introduction of plumbing.



Figure 1. Olmsted Archives circa 1980.

For the first year all documents were processed through the conservation laboratory. After the remodeling of the vault interior was completed, it was possible to adapt an adjacent drafting room to a Phase One working space, greatly increasing output. Now, only badly torn or degraded papers are sent to the conservation laboratory for treatment. Lee Farrow, formerly assistant in the conservation laboratory, designed the Phase I working space around the projected plan storage drawer sizes: 30"x40" (76x102 cm), and 40"x60" (102x152cm). (Plans larger than 40"x60" are stored rolled.) Folders, polyester film,³ and felts were ordered cut to these sizes. Plate glass is 1/4"x20"x30" and for safety reasons may be replaced with 1/2" (13mm) methacrylate sheets.⁴

Phase I Plan Processing

The plans, starting with the older and historically more important, are humidified, unrolled, and inventoried. Each is given a unique number unless it is too fragile to be handled. Each surface of the support is cleaned with a soft, white haired brush. All obvious grime and mold on the verso and edges of the recto is cleaned with grated Mars plastic eraser.⁵ To avoid finger soil, the eraser crumbs are manipulated with a brush or eraser bar. The design area is cleaned very sparingly. At this point lignin content and pH are recorded for future reference.

The 50% RH in the renovated vault is adequate for unrolling most plans. A humidity chamber with 100% RH is used for relaxing plans with undulations and creases before flattening. The first humidity chamber was a tent formed by covering a pair of stainless steel bakery carts with polyethylene sheeting which was humidified by using one or two ultrasonic humidifiers. Unfortunately, its utility was limited by the facts that it took too long for such a large chamber to reach the desired humidity level, that the distribution of humidity within the chamber did not seem to be uniform and that precipitation was occurring inside the tent. A second and much smaller (69"x50"x11") humidification chamber was designed and built for table top use. The basis for its dimensions was the largest storage folder as noted above. It produces a more constant 100% RH and takes up less working space. (Figure 2) Warm tap water (circa 37°C) is poured into a tray in the humidity chamber. The rack was constructed of polyvinylchloride piping with a heat shrinkable polypropylene screening stretched over the top.⁶ Up to ten tracing papers, previously surface cleaned, each supported by a sheet of spunbonded fabric⁷, are then stacked on the rack. The rack is then put into the humidification chamber straddling the tray of warm water (circa 37°C). Polyethylene sheeting is drawn tightly over the top and held in place with bags of lead shot. After five hours, a team of two lifts out each drawing by its support, smooths each between felts, and covers it with plate glass. Since the RH is very low in the room, the polyethylene must be replaced each time a drawing is removed from the chamber. Stacking the plans in the late afternoon leaves the large working tables free for other tasks during much of the day.⁸



Figure 2. Humidity chamber built for Phase I treatment.

The extent of mending is determined by whether or not the plan will be encapsulated in polyester film. If it is, mends are minimal, consisting mostly of tengujo or gampi⁹ and wheat starch paste bridges to keep tears in register. If not, all tears are mended to avoid further damage during handling.

Tracings under 20"x24" are interleaved with buffered tissue and stored unencapsulated, fifteen to twenty in a buffered folder. The interleaving tissues are marked in graphite with the catalog numbers to minimize future handling of the plans. Those over 20"x24" and under 40"x60" are placed on buffered tissue cut to size with windows to reveal verso writing, then encapsulated in polyester film with 3M #415 double-sided tape.¹⁰

Oversized plans remain a dilemma. One mil polyester film encapsulations may ripple when they are rolled and mends tend to reopen. Presently most oversized drawings are rolled onto tubes with a three inch diameter, with up to twelve on each tube interleaved with buffered tissue, and stored inside stacked five inch tubes. Since it was decided to use the historic vault for storage, space is at a premium.

Types of Tracing Paper in the Collection

There are at least five types of tracing paper in the collection possessing widely varying characteristics.¹¹

- A. Resinous - dark to light amber color and very brittle, aromatic.
- B. Parchment like - dense smooth surface, light shades of tan, yellow and white, varying in thickness and transparency.
- C. Matte- more porous surface than "B", usually slightly darker in color.
- D. Same general appearance as "C" with the addition of flecks of groundwood in a cellulose matrix.
- E. Wax paper as in Butcher's, presumably impregnated with paraffin.

None contain lignin except "D" and possibly "E". The vast majority of pH readings fall between 4 and 5.5 with a rare reading of 5.8.¹²

Some of the tracing papers are "transparent" when held in close contact with a substrate; others are not. The latter include many samples that are strong and light in color which suggests that they were used on a light table. The collection contains corresponding sunprints and blue prints, so that once these are cataloged, we may be able to determine how each kind of tracing paper was used.

Only the resinous paper has been analyzed. The fact that many of the others are not permeated by solvents suggest that the "transparency" was achieved by physical means. Jacki Elgar, while a graduate student at the Cooperstown Graduate Program in Conservation¹³, made an infrared spectral analysis of three samples from plans drawn circa 1893. The resin was extracted with acetone and redissolved in chloroform onto potassium bromide pellets and compared to damar and sandarac resins prepared in the same manner.¹⁴ The resin appears to be damar (Figure 3).

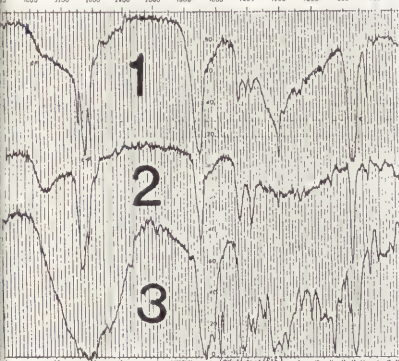


Figure 3.
1. Resin from tracing paper used circa 1893.
2. Damar resin.
3. Sandarac resin.

Of the materials sent to the laboratory for extensive treatment, the most degraded are the resinous tracing papers. They are dark amber in color and very brittle. The rolled paper shatters when compressed as many have been. The resin is soluble in alcohol and more so in acetone.

Removing the resin lightens the color of the support and thereby greatly improves the contrast between the support and the rendering medium. Resin removal increases the suppleness of the support and provides a surface to which adhesives adhere more readily. Resin removal may decrease the transparency of the treated tracing slightly; nevertheless, it becomes easier to see a design through it due to the lighter color. After the resin was removed, sizings of methyl cellulose and Klucel G.¹⁵ were tested to see if they might impart greater transparency to the support. Both tended to darken the support and thereby decrease the visibility of the design.

Treatments

The first resinous tissue treated was a veritable jigsaw puzzle of several hundred small pieces with graphite design which took over a week to assemble. After the resin was removed in three baths of acetone, the fragments were rinsed and deacidified, organized face down on silicone Mylar¹⁶ on a light table and mended with tengujo and wheat starch paste. It was noted that the edges fitted together far better when wet than when dry. The moisture in the mends caused expansion which tended to undo previous mends and to leave tide marks. When fragments were extremely small, it was helpful to lower the mending fibers via a strip of Mylar to avoid displacing them.

Resin impregnated paper is so brittle that it is difficult to unfold without incurring breaks at the folds. To minimize this, we raise the humidity in the laboratory to 65% and may condition the tracing paper in a humidity chamber. We have not yet tried conditioning in solvent vapors or mixed water-solvent vapors. Even though the media of the majority is graphite, we can not increase suppleness by removing the resin prior to unrolling since each must be inspected for solvent soluble media.

The current method of removing the resin from torn, brittle tracings has evolved from an awkward process of submerging them in a tray of solvent to the following production system:

- Unroll tracing on sheet of thin polyester spunbonded fabric.
- Cover with thin blotter.
- Roll with blotter inside.
- Tie with cotton tape.
- Prepare in the fume hood, a thick blotter on which to roll out the tracing and a glass cylinder of solvent. Wear rubber gloves.
- Submerge rolled plan in cylinder of acetone for 30 to 60 seconds while agitating. Blotter may be held with tongs. Reverse and submerge again. In this way it is possible to accommodate rolls longer than the depth of solvent.
- Lift from the cylinder, letting excess solvent drip back.
- Untie tape, unroll quickly on the dry blotter with the thin blotter on top of the tracing.
- Weight perimeter of the blotter with glass weights to maintain contact of blotter with tracing, taking care that weights are not placed over the tracing. At this point the upper blotter is transparent due to the solvent so that the tracing is easily seen below.
- Leave until the blotter is dry. As the solvent evaporates, most of the resin is drawn to the upper surface of the blotter.
- Uneven residues of solvent may be dissolved by brushing on solvent through a blotter and letting dry as above.

Previously used acetone, even when it is already discolored with dissolved resin, seems to remove most of the resin. In practice, when the solvent from the first bath is discolored, we use clean solvent for a second bath.

Once the resin is removed, the paper is quite soft. It is very short fibered, but can be given a standard paper treatment:

- Rinse, face up, on support in deionized water, pH adjusted to 7.5 with $Mg(OH)_2$.
- Soak in Magnesium bicarbonate (We use 0.1 to .02 Molar solutions).
- Drain briefly on screen.
- If fragments are numerous, air dry.

Mending Immediately after Wet Treatment

- If fragments are few in number, place a sheet of silicone Mylar over the top and reverse. The design is now face down.
- Remove supporting fabric.
- Slide the fragments into position. They slide easily on silicone mylar when it is moist. They may be sprayed if they start to dry or blotted to "tack" them down.
- Apply paste to a backing tissue supported on thin spunbonded fabric.
- Lower backing onto plan and brush, squeegee and/or blot to remove bubbles.
- Blot through the supporting fabric, then cover with weighted blotters.
- When partially dry, replace the Mylar with a blotter.

Generally, gampi or tengujo are used with wheat or corn starch paste. The gampi is a more sympathetic color. Care must be taken to match the fiber direction of the backing to that of the drawing, or the backed tissue will roll. Therefore, it is helpful to have wet and dry measurements as it is sometimes difficult to discern the fiber direction. An overall backing on a semi-transparent paper interferes with the original aspect far less than do numerous patches.

When starting with dry fragments, organize them on a support. Plate glass weights are useful to hold them in place. Spray both fragments and silicone Mylar, turn over, realign and back as above. Using this method necessitates being able to keep everything moist with spray until every piece is in place.

Non-Resinous Tracing Papers

We endeavor to avoid wet treatments of tracing papers because not only do most expand considerably across the fiber direction, but also they are extremely difficult to dry without wrinkles and cockles. Expansion tests made on test papers believed to date to about 1930 show an average wet expansion of 3.4% across the fiber direction and 0.3% in the fiber direction. Most dried slightly smaller than the original due possibly to deformation of the surface. Many are composed of such short fibers that any manipulation in the bath may leave stretch puckers.

Experiments with drying on a suction table¹⁷ resulted in uneven drying causing cockles. We attribute this to the lack of porosity of the paper.

Non-Aqueous Deacidification

Once a plan is referred to the laboratory we endeavor to give it a thorough treatment including adjustment of pH. Various Wei T'o non-aqueous preparations¹⁸ have been brushed or sprayed on the plans not receiving wet treatments. Wei T'o cannot be used on resinous tracing papers because the solvents dissolve the resin unevenly. Nor can it be used on waxy papers where it forms a powder on the surface. Other papers react in intermediate ways. On cream and tan colored papers there were problems with it streaking when applied by brush. In most instances it can be acceptably applied by spraying when diluted with a moisture free solvent; we have had success with a fifty percent dilution. Any moisture in the system causes the formation of a gel. This property also necessitates using the solution only on days when the relative humidity is low. Small items may be treated in atmospheres of carbon dioxide or nitrogen in a glove box. The manufacturer will supply the formulations diluted upon request.¹⁹

We noticed that when the solution was applied to one surface only, it was slow to permeate the paper and in some cases remained at the alarmingly high pH of 10 on the side of application.

We therefore conducted a test by applying various Wei T'o solutions to one surface only of a series of blank tracing papers believed to date from the 1930s. pH readings were taken after three months and, in some cases, again after nine months. Records are also being tabulated for the catalogued plans dating from the 1890s which we have deacidified on the verso only. Our statistical analysis of these findings is not yet complete.

Readings were made with non-bleeding surface indicator paper, which visibly indicates any range in pH on any one surface. The pH on the verso, the side of application, was usually one or more units higher than the recto. The indicator paper used on the recto often exhibited a matrix color of one pH with spots of pH one to three units higher.¹²

Removal of Pressure-Sensitive Tapes

Tape removal is difficult because most tracing papers are either not permeable enough to permit solvents to penetrate from the verso or they contain sizings soluble in the solvents needed to remove tape. In the latter case the entire document may be rinsed in solvent providing there are no soluble design elements. Tape encountered on the plans to date seems to be of rather recent origin and to occur most often on large plans. It appears to be 3M Magic Mend, which has the same adhesive as 3M #415 double sided tape which has been tested and reported to have reasonably stable aging characteristics.²⁰ The acetate tape backing is soluble in acetone and the acrylic adhesive gels in various solvents. Removing the gel without damaging the paper is difficult because the fibers are very short and friable. In most cases we use toluene; however, on one brittle tracing paper, amyl acetate seemed to soften the fibers less than did toluene or alcohol, allowing the gel to be scraped off with less effect on the paper surface.²¹

Generally we remove the tape in the design area to avoid any possible long term degradation, but have concluded that in plain areas it appears less damaging to leave the tape in situ than to risk the physical damage of removing it. The other major consideration is that tape removal is very time consuming.²²

The least damaging method of removing this tape is:

- 1- Dissolve the tape backing with acetone and scrape off the resulting gel with a bone or teflon tool.
- 2- Gel the adhesive, (it is not soluble), and remove in the same manner.

Heat Set Tissue Repairs

For repairing the thousands of rips, edge tears and lacunae and for reattaching fragments as soon as their position is located, without the use of moisture, we sought heat set tissue. We required a stable adhesive system that would have no deleterious effect on tracing papers, and would adhere at circa 65°C to avoid heat degradation of the support. We tried tengujo sprayed with Acryloid B72 (ethyl methacrylate copolymer) and Bookmaker's heat set tissue. The latter is commercially prepared with acrylic emulsions following the formula developed by Peter Waters and Margaret Hey.²³ Both of these heat set tissues, even when applied with temperatures greater than 65°C, adhered poorly and unevenly to the tracing papers, especially to those with a waxy appearance (type B), and were easily peeled off. Failure of the mends, with subsequent displacement of fragments, was worst in the case of an oversized plan encapsulated in one mil Mylar and rolled. Both of these tissues were adequate for some papers with matte surface. They were most useful for holding torn fragments in place during polyester film encapsulation of the tracings.

We recently mended a series of large ragged tracing papers (types B and C) with heat set tissue prepared with Beva 371²⁴, which proved satisfactory, adhering well at circa 65°C. The Beva is supplied in a viscous solution which we dilute one to four with ligroin (VMP Naptha), heat in a water bath and spray onto Japanese machine made gampi and tengujo tissue papers. These papers, available in rolls 1"x60", provide ideal backing materials for oversized tracing papers.²⁵ Good results have been obtained with between 40 and 80 mm of solution per meter square of backing tissue. Small backings are sprayed in the fume hood and large backings on an open, outdoor porch on days when the relative humidity is low. The tissue is taped to large wooden racks covered with heat shrinkable polypropylene mesh screens. In either case we wear gas masks and air the paper until the lingering odor of solvent is fully dissipated.

Method of Applying Beva Heat Set Tissue to Oversized Tracing Papers

The Beva on the heat set tissue remains tacky so that it is necessary to face it wherever there is a void. On occasions one may wish to use a facing paper which blends with the support. It should be cut to the exact size to fit the void. In most cases we face the voids with another layer of heat set tissue, applied as follows.

- Place a sheet of silicone Mylar on a light table.
- Arrange the torn document to be repaired, recto uppermost. Weight it in position.
- Slide a large sheet of heat set tissue under the torn end to about a centimeter beyond the deepest tears, tacky side up. The tissue should extend beyond the front edge of the plan to the length of the longest voids, and to the sides to the width of the deepest edge tears. Set tacking iron just hot enough to adhere heat set tissue to document.
- Use silicone Mylar or silicone release paper between the tacking iron and the document.

- At this point, it may be necessary to relax creases and folds with moisture. Often rolling a barely damp swab over the crease followed by drying under a weighted blotter is sufficient. As long as small areas are moistened at a time, there seems to be little deformation. For larger areas, stretching the tracing under a dry blotter with a moist blotter and weight placed on top, may work. Our initial trials with using moisture through Gore-Tex produced puckers; however, we are still exploring its use.
- Work the torn edges of the deepest tear into position and tack to the underlying heat set tissue with the warm tacking iron. Proceed to the remaining tears, smoothing and tacking between tears.
- When all of the backing is firmly adhered to the verso, place colored acetate over the tracing, so that it covers an area larger than the voids.
- Fold the heat set tissue evenly over the recto, with the fold at right angles to the sides of the drawing, so that the heat set tissue covers the voids.
- With a scalpel cut the overlapping heat set tissue to cover each void, allowing several centimeters overlap onto the document.
- Remove the acetate sheet and iron the heat set tissue into place on the recto.
- At the side margins, fold the heat set tissue over the tracing to cover the worst of the edge tears. The corners may be mitered to avoid a triple thickness of backing tissues.
- Continue repairing the document edges, with folded strips of tissue.

We feel that a folded mending tissue is much stronger and less likely to come apart than two separate sheets of heat set tissue. A double layer of the thin tengujo (5.7g/m^2) is soft and easy to roll. In cases where a stronger or thicker backing paper is needed, a thin paper may still be used on the recto and folded over the verso to provide edge protection.

We seldom back the whole plan, for several reasons: the long range aging properties of Beva on various tracing papers is unknown, spraying the backing tissue is time and space consuming and the materials are expensive.

Conclusion

The sheer magnitude of the problem of providing researchers access to a large collection of uncatalogued rolled documents of varying sizes and supports, presently in poor physical condition, is stimulating new approaches to processing, treatment and storage. We are always searching for better solutions to half-solved problems such as the flattening of badly torn tracing papers. With knowledge gained from future analyses of each type of tracing paper, we will be able to proceed with greater understanding. Condition-treatment records generated by the Phase I staff will enable the conservator to return to documents that require further treatment as methods are perfected and time allows. Our goal remains to provide conservation quality storage and, when time permits, treatment of each document.

Notes

- 1- Parks designed by F.L.Olmsted: Central Park, New York City; U.S. Capitol Grounds, Washington, D.C.; Stanford University campus and Boston Park System.
2. The Curator, the Conservator, the Archivist and four Technicians are the only staff members involved with handling or treating archival materials.
3. Mylar D and Melinex 516 are polyester films composed of oriented polyethylene terephthalate. Their stability and transparency make them suitable for use with archival materials.
4. Plexiglas, Oroglass and Perspex are trade names for methacrylate sheets.
5. Mars Plastic vinyl erasers are manufactured by Staedtler, Nurnberg, Germany.
6. Heat shrinkable screening is produced by Chikopee Mfg. Co., Cornelia, Georgia and by Tetko, Inc., which has headquarters in Switzerland and distributors in Elmsford, N.Y. In Canada it is handled by B.& S.H. Thompson & Co.
7. We are using Hollytex spunbonded polyester and Cerex spunbonded nylon. The former exhibits less dimensional change when wetted than the latter.
8. Materials used to build the humidity chamber were Plexiglas, PVC piping, heat shrinkable screen, and foam pipe insulation atop the rim to achieve a tight seal with the polyethylene cover. The only difficulty encountered was locating an adhesive that would adhere to both the PVC piping and the polypropylene screening. The tray was purchased from Totline, Molded Fiberglass Tray Co., Linesville, PA 16424, USA.
9. Tengujo is a thin, long-fibered Japanese tissue composed of mulberry bast fibers. Gampi, composed of bast fibers from a shrub of the same name, is crisp, thin, more dense and strong.
10. We considered an ultrasonic sealer, but because of space and financial constraints combined with the fact that many of our plans are larger than the sealing units on the market, we remain with the easily reversible tape.
11. The only watermark found was on a plan dated 1880. It is identical to the one published by Sally Anne Yates. Ms. Yates noted that she had observed no insect damage. The only insect damage that we have encountered was silverfish gnawings on mold damaged specimens.
12. pH readings are taken with non-bleeding, surface pH indicator strips manufactured by Macherey-Nagel GMBH & Co. of Duren or by E. Merck, Darmstadt, F 12 Germany.
13. The former "Cooperstown Graduate Program in Conservation of Historic and Artistic Works" is now "Art Conservation Department", State University College at Buffalo, New York..
14. The samples used for comparison were: Singapore Damar #1 from Permanent Pigments, Cincinnati, Ohio and Sandarac from A.F. Suter & Co., Ltd.
15. Klucel G is hydroxypropylcellulose, manufactured by Hercules Incorporated, 910 Market Street, Wilmington, Delaware 19899, USA.
16. The silicone coating on the silicone Mylar is so smooth that it is useful as a drying support for papers during treatment permitting them to expand or contract. In addition, it does not adhere well to adhesives.
17. Our suction table was designed by Nascor Technical Services Box 706, Sag Harbor, Long Island, NY 11963, USA.
18. The following are the non aqueous solutions we have used. The first number denotes a bottled liquid, the second a solution in a pressurized spray can:
Wei T'o #2 and #10- Methyl magnesium methyl carbonate in trichlorotrifluoroethane and methanol.
Wei T'o #3 #11- ethoxy magnesium ethyl carbonate in trichlorotrifluoroethane and ethanol denatured with methanol.
Wei T'o #4 #12- Same as #3 with a greater proportion of ethanol.
We are discontinuing the use of the methanol solutions because we are informed that organic respirator filters do not remove methanol. (Monona Rossol, The Center for Occupational Hazards, 5 Beekman St. New York NY 10038, in a lecture given to the New England Conservation Association on November 19, 1986.)

19. Personal communication, Richard D. Smith, President, Wei T'o Associates, Inc., P.O. Drawer 40, Matteson, IL 60443, USA.

20 and 21- See Smith 1984.

22. Spraying a plan with Wei T'o puckered the tape, necessitating its subsequent removal.

23. See Waters 1977. The heat set tissue is available from Bookmakers 2025 Eye Street, N.W., Washington, D.C., USA.

24. Beva is available from Adam Chemical Co, Inc, 18 Spring Hill Terrace, Spring Valley, N.Y. 10977, USA. The preformed film sold is far too thick for use with tracing papers. It tends to sink into the tracing paper, changing the transparency.

25. Paper NAO, 1-29-12-201 Senoku Bunkyo-ku, Tokyo 112, Japan. Its use was reported by T. K. McClintock at the conference, "New Directions in Paper Conservation", Oxford, 1986.

26. Gore-Tex barrier laminates are waterproof but vapour permeable. W.L. Gore & Associates, Inc. Gore-Tex Fabric Division, Box 1130, Elkton, Maryland 21921, USA.

Bibliography

Konstanze Bachman, "The Treatment of Transparent Papers: a Review", The Book and Paper Group Annual, Vol 2, American Institute for Conservation of Historic and Artistic Works, Washington D.C., 1983, pp, 3-14.

Konstanze Bachman, "Transparent Papers before 1850: History and Conservation Problems", New Directions in Paper Conservation, Preprints of The Institute of Paper Conservation 10th Anniversary Conference, 14-17 April, 1986, Oxford, England, p. D51.

Andrew Bush, "Conservation of 19th Century Tracing Papers in the National Maritime Museum", New Directions in Paper Conservation, Preprints of The Institute of Paper Conservation 10th Anniversary Conference, 14-17 April, 1986, Oxford, England, pp. D61-62.

Thomas K. McClintock, "The Drawings of Frank Lloyd Wright: Conservation of the Works on Tracing Paper", New Directions in Paper Conservation, Preprints of The Institute of Paper Conservation 10th Anniversary Conference, 14-17 April, 1986, Oxford, England, pp. D63-64.

John S. Mills, "Analysis of Some 19th Century Tracing Paper Impregnants and 18th Century Globe Varnishes", New Directions in Paper Conservation, Preprints of The Institute of Paper Conservation 10th Anniversary Conference, 14-17 April, 1986, Oxford, England, pp. D62-63.

Laura Wood Roper, FLO, A Biography of Frederick Law Olmsted, The Johns Hopkins University Press, Baltimore and London, (1983) pp. 555.

Christopher D. Rundle, "The Composition and Manufacture of Modern Tracing Papers", New Directions in Paper Conservation, Preprints of The Institute of Paper Conservation 10th Anniversary Conference, 14-17 April, 1986, Oxford, England, pp. D64-65.

Merrily A. Smith, Norvell M.M. Jones, II, Susan L. Page and Marion Peck Dirda, "Pressure Sensitive Tape and Techniques for its Removal from Paper," Journal of the American Institute for Conservation, Vol. 23, #2, (Spring 1984), pp. 101-113.

Peter Waters and Margaret Hey, "Heat Set Tissue Preparation and Application", Conservation Workshop Notes on Evolving Procedures, Series 300, No. 1, Library of Congress Publications on Conservation of Library Materials, May 1977.

Sally Ann Yates, "The Conservation of Nineteenth Century Tracing Paper", The Paper Conservator, Vol. 8, 1984, pp. 20-29.

RESUME

Des recherches ont été faites sur l'action éventuelle des sels de plomb pouvant être absorbés par le papier en présence d'une pollution atmosphérique causée principalement par la combustion des essences contenant des additifs à base de plomb. Les concentrations de plomb des papiers utilisés couramment pour la restauration des matériaux de bibliothèque ont été calculées au moyen du spectrophotomètre à absorption atomique. Deux traitements avec de l'acétate de plomb ont été testés sur des papiers échantillons (Whatman n.1 et type "Journal"), carbonatés ensuite à l'air et lavés à l'eau courante: l'un avec une concentration comparable à la moyenne des valeurs rencontrées dans le papier utilisé habituellement et l'autre avec une concentration mille fois supérieure. Pour contrôler la stabilité de ces papiers aux vieillissements accélérés (105°C; 80°C et 80% H.R.; 90°C et 78% H.R.), on a mesuré les variations de la blancheur, du pH et des spectres IR. De plus pour le papier Whatman on a mesuré le degré de polymérisation. La présence de plomb aux concentrations testées ne semble pas altérer de façon substantielle la stabilité des papiers examinés.

INFLUENCE DU CONTENU EN PLOMB SUR LA CONSERVATION DU PAPIER

Mariagrazia Plossi Zappalà
Istituto Centrale per la Patologia del Libro
Laboratorio di Chimica
Via Milano 76
00184 Rome
Italie

Antonio Zappalà
Istituto Nazionale per la Grafica
Laboratorio Scientifico
Via della Lungara 230
00165 Rome
Italie

Introduction

Le plomb est une des substances polluantes les plus préoccupantes, particulièrement lorsque sa concentration augmente dans l'air, dans le sol et dans les eaux, surtout dans les régions urbaines.

De nombreux auteurs ont démontré que dans l'atmosphère il y a actuellement une concentration trente fois supérieure à celle mesurée avant le développement industriel (1,2,3).

Le plomb, contenu dans les essences (plomb tétraméthyle et tétraéthyle) et ensuite présent dans l'atmosphère sous forme d'aérosol, est le plus grand responsable de la pollution atmosphérique en plomb. Le plomb dans les essences a commencé à être utilisé en 1923. Comme pour les autres substances polluantes, on a trouvé dans l'air et dans le sol une concentration plus forte près des routes à circulation intense. En outre la concentration dans le sol est directement proportionnelle à leur date de construction (4).

On peut voir dans le tableau I quelques exemples de concentration de plomb due à la pollution atmosphérique tels que nous les avons trouvés dans la littérature (5,6,7,8,9,10,11,12).

Tableau I

Concentration en plomb dans:

Roches cristallines et sédimentaires	de 0.1 à 20 ppm
Sol pollué	de 110 à 700 ppm
Poussière (Zurich) (1963)	2.04%
Air (Zurich) (1963)	2.8 g/m ³
Air (Paris) (1963)	de 5.0 à 9.8 g/m ³
Conifère (pollution variable) (Suède, 1967)	de 5 à 700 ppm

L'information la plus importante pour notre sujet est que la concentration dans les conifères, dont le bois est utilisé pour la fabrication de la cellulose chimique, peut être très forte (12). Par conséquent, comme l'a suggéré le Prof. E. Chiacchierini, Directeur de l'Istituto di Merceologia de l'Université de Rome, le Pb pourrait être présent dans de nombreux papiers préparés avec de la cellulose dérivée du bois.

En ce qui concerne le coton, et par conséquent les papiers qui sont fabriqués à partir de ce matériau, on peut supposer qu'il en contient une concentration assez faible car les cultures sont placées loin des routes.

Selon certains, le plomb présent dans les aérosols joue aussi le rôle de catalyseur de l'oxydation en milieu aqueux de l'anhydride sulfureux et par conséquent pourrait accélérer la dégradation de la cellulose (13,14,15,).

N. Hon (16) a d'autre part démontré que le plomb peut favoriser la dégradation de la cellulose dans ses parties amorphes avec la formation de radicaux lorsqu'elle est exposée à des radiations ultraviolettes. Le même auteur a pu constater que la formation de ces radicaux ne se produit pas avec des radiations d'une longueur d'onde supérieure à 3300-3400 Å.

Il nous a donc semblé intéressant de vérifier aussi l'éventuelle action des sels de plomb sur la stabilité du papier soumis à un vieillissement accéléré avec augmentation de la température et de l'humidité relative.

Les résultats de ce travail pourront permettre d'évaluer l'opportunité d'ajouter aux Normes du Ministère Italien des Biens Culturels (normes qui fixent les caractéristiques minimales de qualité des papiers à utiliser pour la restauration des livres) le contrôle de la présence de ce métal (17).

Le but de notre recherche sera donc:

- la détermination de la concentration en plomb dans différents papiers modernes;
- l'évaluation de l'effet sur un papier en cellulose pure (Whatman n.1) et sur un papier de type "journal" (contenant un pourcentage élevé de pâte de bois) d'une concentration de plomb comparable à celle normalement trouvée dans les papiers modernes;
- l'évaluation de l'effet sur les deux mêmes types de papier d'une concentration environ mille fois supérieure.

Détermination de la teneur en plomb dans quelques papiers modernes

Le plomb a été mesuré sur des papiers utilisés pour la restauration des livres, sur un papier de cellulose pure (Whatman n.1) et sur un papier ayant une concentration élevée de pâte mécanique de bois (voir tableau II).

Tableau II

Caractéristiques des papiers examinés

- 1- Papier japonais n.502 (Oskar Vangerow) employé pour le doublage des documents fragiles (pH=6.6, réserve alcaline=0.15%, manille=100%, Fe=24 ppm)
- 2- Papier Whatman n.1 pour chromatographie (cellulose de coton avec le 98% de α -cellulose, pH=6.0)
- 3- Carton "Durevole per la conservazione" (Cartiere Miliani, Fabriano) fabriqué selon la Norme du Ministère Italien pour les Biens Culturels, Décret du 2 août 1983, utilisé pour la reliure des livres restaurés et comme passe-partout de gravures et des sins (linters de coton=100%, réserve alcaline=2.5%, pH=8.40)
- 4- Papier japonais n. 511 (Oskar Vangerow) employé dans la restauration des livres pour le traitement des lacunes (pH=6.6, conifère=70% et manille=30%, Fe=70ppm)
- 5- Carton "Cagliari" autrefois utilisé en reliure.
- 6- Papier "Journal" (Ente Nazionale Cellulosa e Carta, Rome) (pâte blanchie à la soude de conifère=70%, pâte mécanique de bois de conifère=30%, colophane=0.35%, alun=30%, kaolin=10%, pH=6.5)

Une quantité mesurée de chaque échantillon a été incinérée selon la norme ATICELCA MC 14/68 qui conseille la combustion du papier à 525°C dans un four à moufle.

La teneur en cendres (pourcentage p/P) figure dans le tableau III.

Les cendres ont été ensuite traitées dans une capsule de silice avec 2 cm³ d'acide nitrique (1:3 en volume) et desséchées par chauffage; après avoir ajouté trois fois 1 cm³ d'acide nitrique (1:3), on est arrivé à 10 cm³ avec le même acide nitrique. Le

Prof. G. Fonseca de l'Istituto di Merceologia de l'Université de Rome a déterminé le contenu en plomb de ces solutions avec le spectrophotomètre à absorption atomique. La teneur de plomb déterminée dans ces éprouvettes figure dans le tableau III.

Tableau III

Pourcentage des cendres et de la concentration en plomb (ppm par rapport au poids du papier sec)

Papier	Cendres	Pb
1 (502)	0.64%	0.008 ppm
2 (Whatman n.1)	0.09%	0.009 ppm
3 (Carton Miliani)	2.68% (2% CaCO_3)	0.030 ppm
4 (511)	0.60%	0.039 ppm
5 (Carton Cagliari)	23.13%	1.638 ppm
6 (Journal)	0.41%	0.032 ppm

On peut voir que la concentration est très basse dans le papier japonais pour doublage et naturellement dans le papier Whatman.

La concentration en plomb est au contraire 200 fois plus élevée dans le carton Cagliari qui, heureusement, n'est plus employé pour la restauration des livres depuis que le Ministère Italien des Biens Culturels a publié un décret interdisant l'emploi pour la restauration des matériaux soumis à la tutelle de l'Etat Italien, de carton ayant des caractéristiques qualitatives inférieures à celles prévues par le décret (17). On peut remarquer qu'un quart du poids du carton Cagliari est formé par des substances incombustibles.

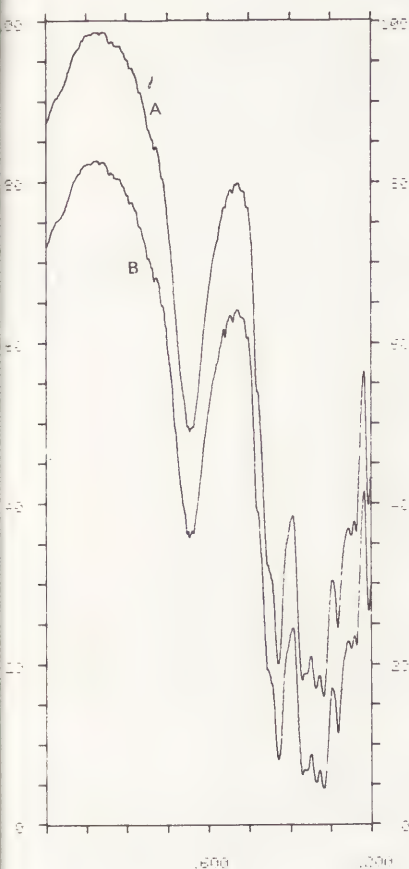


Fig.1 Spectre A: papier Whatman non traité

Spectre B: papier Whatman non traité et vieilli à 90°C et 78% H.R. pendant 60 jours

Les spectres inférieurs ont été déplacés de 15% sur l'axe des ordonnées

Effet de la teneur en plomb sur la stabilité et par conséquent sur la conservation du papier

Afin de mesurer l'effet du plomb, nous avons effectué deux traitements sur papier Whatman et papier "journal":

T1: immersion dans une solution d'acétate de plomb contenant 0.001 g/l de plomb. Les éprouvettes traitées ont été exposées à l'air pendant cinq jours afin de transformer l'acétate de plomb en carbonate très peu soluble dans l'eau. Ensuite les éprouvettes ont été rincées dans l'eau courante pendant trois heures pour enlever le résidu d'acétate de plomb soluble encore présent. La teneur moyenne en plomb déterminée avec le spectrophotomètre est de 0.12 ppm.

T2: immersion dans une solution d'acétate de plomb 1000 fois plus concentrée. Le contenu moyen de plomb, après la même exposition à l'air et le même rinçage, est de 87 ppm.

Une partie des éprouvettes, traitées et non traitées, a été vieillie à sec dans une étuve à 105°C.

Une autre partie a été vieillie à la chaleur humide (80°C et 80% H.R.).

Une troisième partie a été vieillie à 90°C et 78% H.R.

Afin de vérifier le comportement du papier Whatman, nous avons mesuré le degré de blancheur, le pH et le degré de polymérisation, et le spectre IR sur le papier non traité et traité avec les deux solutions d'acétate de plomb, soumis ou non au vieillissement artificiel.

Sur le papier "journal", nous avons effectué les mêmes mesures excepté le degré de polymérisation à cause de l'impossibilité de solubiliser le papier dans la solution de cupriéthylendiamine

due à la présence d'un contenu élevé de lignine.

Pour la mesure du pH, nous avons utilisé le titreur automatique Radiometer PH M82 Standard pHmeter, conformément à la norme TAPPI T 435 m-52 (extraction à froid avec de l'eau distillée).

Pour le degré de blancheur, nous avons utilisé le Photoelectric Reflection Meter 610, Photovolt Co., avec l'unité de recherche 610-W, conformément à la norme TAPPI T 442 m-48.

Pour le degré de polymérisation moyen viscosimétrique, nous avons utilisé la norme AFNOR NF 12-005.

Pour le spectre IR, nous avons utilisé le Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer, dont la grande sensibilité nous a permis d'effectuer les spectres sur des échantillons sans devoir inclure le papier dans des pastilles de KBr.

Les résultats de tous ces essais figurent dans les tableaux IV, V, VI, VII, VIII et dans les figures 1, 2, 3 et 4.

Discussion des résultats

Le résultat le plus rassurant, et qui peut faire supposer que la pollution due au plomb ne provoque aucune accumulation de ce métal dans la cellulose, est que dans le papier de bonne qualité la concentration en est en effet basse (tableau III). Le taux élevé trouvé dans le carton Cagliari est sans doute dû au haut pourcentage de charges minérales.

En ce qui concerne le pH (tableau V et VIII), on remarque que les échantillons traités présentent des valeurs légèrement plus élevées que celles des non traités et qu'en général cela persiste même après les vieillissements accélérés. On a également noté que durant ces mesures, les échantillons traités se mouillent avec plus de difficultés; le phénomène est particulièrement évident avec le papier "journal".

Le degré de blancheur (tableau IV et tabl. VII) n'est pas sensiblement modifié par les traitements. Les échantillons de papier Whatman qui, à la suite du vieillissement, avaient subi un jaunissement plus prononcé (c'est-à-dire les échantillons vieillis à sec à 105°C), ont été lavés à l'eau courante pendant trois heures; leur degré de blancheur a augmenté après lavage d'environ 5%, ce qui pourrait faire supposer que pendant le vieillissement à sec (aussi bien pour les échantillons traités que pour ceux non traités), il y ait eu production de fractions colorées d'un poids moléculaire bas, solubles dans l'eau, comme l'ont déjà constaté d'autres auteurs (18).

En ce qui concerne le degré de polymérisation, on remarque que, tandis que dans le cas du vieillissement à sec une légère dépolymérisation des échantillons traités par rapport à ceux non traités se produit (supérieure de peu aux limites de l'erreur expérimentale), le traitement apparaît stabilisant dans le cas du vieillissement à 90°C et 78% H.R., même si c'est d'une façon légère.

Cette différence de comportement pendant le vieillissement à sec par rapport à celui en milieu humide a été déjà vérifié en présence d'autres ions bivalents (19,20): le calcium et le magnésium produisent le même phénomène sur le papier Whatman, c'est-à-dire un papier de cellulose pure qui n'a pas été déionisée avec des acides avant d'être soumise à des traitements.

En tout cas les résultats expérimentaux obtenus jusqu'à présent indiquent que les vieillissements en milieu humide peuvent être considérés comme les plus sûrs et susceptibles d'être confrontés avec le vieillissement naturel.

En ce qui concerne les spectres IR (fig. 3 et 4) sur le papier "journal", tandis que l'on peut noter des différences dues au

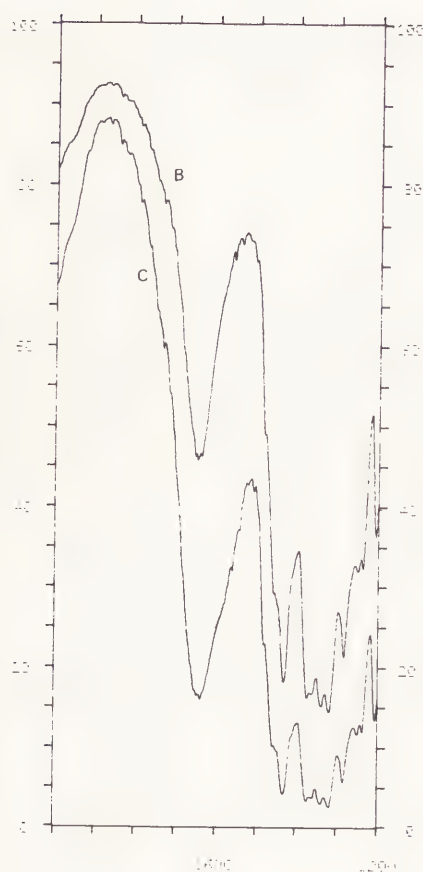


Fig. 2 Spectre B: papier Whatman non traité, vieilli à 90°C et 78% H.R. pendant 60 jours

Spectre C: papier Whatman traité T2 et vieilli à 90°C et 78% H.R. pendant 60 jours

Les spectres inférieurs ont été déplacés de 15% sur l'axe des ordonnées.



Fig. 3 Spectre A: papier journal non traité

Spectre B: papier journal non traité et vieilli à 90°C et 78% H.R. pendant 45 jours

es spectres inférieurs ont été déplacés de 30% sur l'axe des ordonnées.

vieillissement, on ne remarque pas de différences significatives provoquées par les traitements: la bande à 1730- 1725 cm^{-1} (correspondante au CO-stretching des acides carboxyliques) (21) et la bande à 1600 cm^{-1} (correspondante au ion COO^-) (21), s'élargissent après le vieillissement de la même façon pour les échantillons traités que pour ceux non traités. Sur le papier Whatman (fig. 1 et 2), on ne remarque même pas ces différences entre les échantillons vieillis et ceux non vieillis: très probablement la très faible quantité de carbonyles présents dans le papier Whatman fait que leur oxydation en carboxyles due au vieillissement accéléré ne suffit pas à modifier le spectre IR. L'élargissement de la bande à 1600 cm^{-1} sur le spectre du traité T2 est peut-être à attribuer à une légère augmentation des COO^- , sans que l'on puisse simultanément remarquer une diminution du degré de polymérisation du papier Whatman traité par rapport à celui non traité. La compréhension de ce phénomène pourrait être intéressante à approfondir par des recherches ultérieures.

En conclusion, en l'état actuel des recherches, il n'apparaît pas que le traitement avec de l'acétate de plomb (carbonaté à l'air) modifie de façon substantielle la stabilité du papier de cellulose pure (Whatman n;1), ni celle du papier contenant de la pâte de bois ("journal"), lorsqu'ils sont soumis à des vieillissements accélérés à haute température et humidité.

Tableau IV

Effet du contenu de plomb sur le degré de blancheur (± 1) du papier Whatman

	non vieilli	jours de vieilliss. à 105°			jours de vieilliss. à 80° et 80% H.R.				jours de vieilliss. à 90° et 78% H.R.		
		15	30	60	15	30	60	120	15	30	60
A	89	84	80	75	88	88	87	84	86	84	82
B	88	84	80	75	88	88	87	85	86	85	82
C	88	84	80	75	88	88	87	85	84	85	83

A = non traité

B = T1 (Pb 0.12ppm)

C = T2 (Pb 87 ppm)

Tableau V

Effet du contenu de plomb sur le pH (± 0.5) du papier Whatman

	non vieilli	jours de vieilliss. à 105°			jours de vieilliss. à 80° et 80% H.R.				jours de vieilliss. à 90° et 78% H.R.		
		15	30	60	15	30	60	120	15	30	60
A	6.0	5.8	5.5	5.2	5.7	5.7	5.4	5.3	5.6	5.5	5.3
B	6.4	6.2	6.1	5.8	6.1	6.2	6.2	6.2	6.2	6.4	6.2
C	6.5	6.3	6.2	6.1	6.0	6.0	6.0	6.0	6.1	6.2	6.0

A = non traité

B = T1 (Pb 0.12ppm)

C = T2 (Pb 87ppm)

Tableau VI

Effet du contenu de plomb sur le degré de polymérisation moyen viscosimétrique ($\eta_P \pm 50$) du papier Whatman

	non vieilli	jours de vieill. à 105°			jours de vieill. à 80°, 80% H.R.				jours de vieill. à 90°, 78% H.R.		
		15	30	60	15	30	60	120	15	30	60
A	1320	880	695	555	1230	1220	1210	1010	1195	1100	760
B	1300	750	625	470	1230	1230	1180	1030	1190	1124	860
C	1310	755	650	480	1225	1230	1148	1035	1189	1080	820

A = non traité B = T1 (Pb 0.12 ppm) C = T2 (Pb 87 ppm)

Tableau VII

Effet du contenu de plomb sur le degré de blancheur (± 1) du papier "journal"

	non vieilli	jours de vieilliss. à 105°				jours de vieill. à 80° et 80%H.R.				jours de vieill. à 90° et 78%H.R.			
		6	14	30	45	6	14	30	45	6	14	21	30
A	47	46	46	41	37	41	39	38	32	36	31	29	24
B	49	48	46	42	39	42	38	35	34	35	30	26	23
C	45	43	42	41	39	42	40	38	34	39	31	22	22

A = non traité B = T1 (Pb 0.12ppm) C = T2 (Pb 87ppm)

Tableau VIII

Effet du contenu de plomb sur le pH (± 0.5) du papier "Journal"

	non vieilli	jours de vieilliss. à 105°				jours de vieill. à 80° et 80% H.R.				jours de vieill. à 90° et 78% H.R.			
		6	14	30	45	6	14	30	45	6	14	21	30
A	6.5	6.5	6.3	6.0	5.7	6.2	6.0	5.6	5.5	5.8	5.4	5.0	4.9
B	6.5	6.4	6.4	5.8	5.6	6.1	5.9	5.5	5.4	5.6	5.3	5.0	4.9
C	6.6	6.5	6.5	6.3	6.2	6.2	6.4	6.1	5.9	6.0	5.7	5.1	4.7

A = non traité B = T1 (Pb 0.12 ppm) C = T2 (Pb 87 ppm)

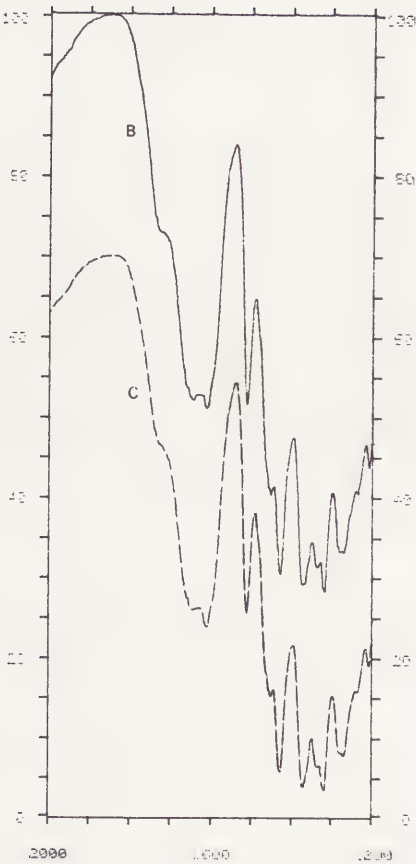


Fig. 4 Spectre B: papier journal non traité, vieilli à 90°C et 78% H.R. pendant 45 jours.

Spectre C: papier journal traité T2 et vieilli à 90°C et 78% H.R. pendant 45 jours.

Les spectres inférieurs ont été déplacés de 30% sur l'axe des ordonnées.

Bibliographie

- 1) PATTERSON, C.C., Arch. Environ. Health, 11, 334 (1965).
- 2) PATTERSON C.C., "Lead" in "Impingement of man on the Oceans", Hodd D. ed., Wiley (1970).
- 3) GANDUSSIO, R., Annali Ist. Sperim. Nutrizione delle Piante, Sez. operativa periferica di Gorizia, 1, 229 (1971).
- 4) SINGER, M.J. et HANSON, L., Soil Sci. Soc. Amer. Proc. 33, 152, (1969).
- 5) GOLDSCHMIDT, V.M., "Geochemistry", Clarendon Press, Oxford (1954).
- 6) CANNON, H.L. et BOWLES, J.M., Science, 137, 765 (1965).
- 7) CHOW, T.J., et PATTERSON, C.C., Geochim. Cosmochim. Acta, 26, 263 (1962).
- 8) VINOGRADOV, A.P., Geochimie, 1, 6-52 (1956).
- 9) HUFF, L.C., Econ. Geol., 46, 524-540 (1951).
- 10) KENNEDY, V.C., Circ. U.S. Geol. Surv., 168, 15 (1952).
- 11) TUREKIAN, K.K. et WEDEPHOL, K.H., Bull. Geol. Soc. Amer., 72, 175 (1961).
- 12) KELLER, Th., et PRESIS, H., Schweiz. Z. Forstwesen, 118 (3), 143-162 (1967).
- 13) URONE, P., et autres, Environ. Sci. Technol., 2, 611 (1968).
- 14) BUFALINI, M., Environ. Sci. Technol., 5, 685 (1971).
- 15) CHAINE, C., et LEROY, M., "Effet de la pollution atmosphérique sur le cuir et le parchemin" in "Les documents graphiques et photographiques: analyse et conservation", Travaux du Centre de Recherches sur la Conservation des Documents Graphiques, édition du CNRS, 71-92 (1980-81).
- 16) HON, N., J. Polym. Sci., Polym. Chem. ed., 13, 1933 (1975).
- 17) ZAPPALÀ, A., Boll. Ist. Centr. Patol. Libro, 37, 73-102 (1981). Decreto Min. Beni Culturali Ambientali du 2 août 1983, "Approvazione della normativa in materia di cartoni destinati al restauro ed alla conservazione del materiale soggetto a tutela", Gazz. Uff. della Repubblica Italiana, 257, 19 septembre 1983.
- 18) MENACHEM, L., et ZIDERMAN, I., Cellulose Chem. Technol. 14, 743-47 (1980).
- 19) SANTUCCI, L., Boll. Ist. Centr. Patol. Libro, 32, 73 (1973-74).
- 20) ROSSI, L. (candidato), SANTUCCI, L. (relatore), "Influenza della concentrazione ionica e dell'acqua adsorbita sulla velocità di degradazione di cellulosa contenente carbonati alcalini e alcalino-terrosi", tesi di Laurea in Chimica, Università degli Studi di Roma, anno accademico 1983-84.
- 20) MARTON, J., et SPARKS, H.E., TAPPI, 50, n.7, 363-68 (1967).

Remerciements

Nous remercions le Prof. E. Chiacchierini et le Prof. G. Fonseca de l'Istituto di Merceologia de l'Université de Rome pour leurs conseils et leur aide pendant notre recherche.

Un remerciement particulier va à notre collègue et ami Paolo Calvini pour les discussions utiles et l'aide pour les examens aux IR, et à Monsieur G. Zaccaria pour l'exécution de certaines mesures.



Working Group 15

Mural Paintings and Mosaics

Peintures murales et mosaïques



ACTIVITES DU GROUPE DE TRAVAIL "PEINTURES MURALES ET MOSAIQUES"

Bilan Triennal

Marcel STEFANAGGI, Coordinateur (France)
Eudald GUILLAMET, Coordinateur adjoint (Andorre)

Le groupe de travail "Peintures Murales et Mosaïques" s'est réuni lors du congrès de COPENHAGUE, en septembre 1984. Lors de cette réunion (relativement restreinte), ont été définies les premières lignes d'un programme :

- . expériences de chantier
- . études de laboratoire
- . applications in situ

Par la suite, le groupe s'est réuni à CHAMPS-SUR-MARNE (FRANCE) au Laboratoire de Recherche des Monuments Historiques en 1985 et 1986. A la date de la rédaction de ce texte, d'autres réunions sont prévues en ANDORRE/BARCELONE les 20 et 21 mai 1987 et fin novembre à CHAMPS-SUR-MARNE ou à LONDRES. D'une façon générale, le groupe a décidé de se réunir chaque année fin novembre.

Ces réunions ont rassemblé une dizaine de personnes (ALLEMAGNE, ANGLETERRE, AUTRICHE, FRANCE, ITALIE, SUISSE). Elles étaient consacrées d'une part à des exposés des différents participants concernant leurs travaux, d'autre part à des discussions sur un certain nombre de problèmes concernant les peintures murales et leur conservation. D'autres membres du groupe ont adressé des contributions par courrier (DANEMARK, HONGRIE, U.R.S.S.).

Les sujets traités sont assez disparates, compte tenu de la diversité spécifique à la peinture murale et à la mosaïque (ou techniques apparentées).

Sans faire une énumération exhaustive, les principaux problèmes sont :

- . les problèmes liés à l'architecture et l'environnement
- . les problèmes des anciennes restaurations, donc de dé-restauration, auxquels on peut rattacher les problèmes d'ordre éthique et esthétique
- . les problèmes des produits employés (solvants, fixatifs), auxquels se rattachent les questions de sécurité (toxicité, etc..).

Ont été également abordés des sujets jusqu'ici peu étudiés, tels que la conservation des surfaces peintes architecturales (notamment dans l'architecture baroque).

Tout en maintenant le principe d'exposés réguliers par les membres du groupe sur des sujets de leur choix, il a été décidé, compte tenu de la disparité des sujets d'étude, de travailler sur des thèmes précis qui, s'ils ne sont pas prioritaires, ont l'avantage de pouvoir faire l'objet d'un travail concret, en raison de leur caractère général.

Ce sont :

- . la sécurité : problème d'emploi des solvants, conditions exactes à respecter. Certains produits devraient-ils être limités en emploi ? Inversement, à partir de quelles limites un produit est-il dangereux ? Un état de la question doit être établi pour les différents pays en vue d'une synthèse globale qui pourrait constituer une information générale
- . la nomenclature : le groupe étudie la possibilité d'établir d'abord un glossaire multilingue (ALLEMAGNE, FRANCE, GRANDE-BRETAGNE, ITALIE) de la terminologie. Celle-ci est en effet souvent sujette à confusion, et peut constituer une source d'erreurs, surtout quand on passe d'une langue à l'autre. L'objectif serait ensuite de mettre en oeuvre un projet de normalisation des termes et des symboles utilisés pour les descriptions et les relevés des peintures et de leurs altérations. Ce travail pourrait éventuellement faire l'objet d'une publication "ICOM".

La variété des préoccupations est donc une des caractéristiques principales du groupe. Elle est due essentiellement au fait que les problèmes de peinture murale et de mosaïque sont des problèmes de terrain, et non des problèmes de musée comme c'est le cas pour la plupart des groupes. Il faut donc noter à ce sujet l'importance primordiale de la collaboration restaurateur/historien d'art/scientifique (et éventuellement architecte), collaboration qui n'est pas toujours une réalité : beaucoup de restaurateurs travaillent souvent dans un contexte restreint et sont souvent ignorants de l'histoire des restaurations.

D'une façon générale, il y a lieu de souligner l'intérêt que suscitent les réunions du groupe en dehors de celles des congrès tous les 3 ans, ainsi que la circulation de l'information et des échanges de vue. En effet, même si la plupart des membres restent en contact régulier par courrier, cela ne peut remplacer les discussions de vive voix, qui occupent généralement une longue journée et se prolongent souvent dans la soirée de façon informelle.

Les réunions ont pu également être élargies en y invitant certains participants extérieurs au groupe, en liaison notamment avec le groupe "peinture murale" de la S.F.I.I.C (Section Française de l'Institut International de Conservation). Enfin, rappelons que le groupe était représenté à la conférence générale de BUENOS AIRES, où il a présenté un poster.

En mars 1987, le groupe compte 35 inscrits, dont 23 participent effectivement aux travaux du groupe (réunions, contributions écrites, publications).

Résumé

L'argument de ce texte est la méthodologie élaborée et l'effective réalisation de la séparation d'une peinture à huile sur mur d'une peinture à fresque sous-jacente. Cette intervention a été réalisée par les techniciens de l'Opificio delle Pietre Dure de Florence sur une peinture de Andrea Lilli dans le cloître de l'ancien couvent de Sant'Angelo Magno à Ascoli Piceno.

Pour assurer la réussite de l'opération, nous avons dû établir quelques variations à la technique habituelle. De telles variations n'ont pourtant pas requéri des matériaux différents de ceux communément utilisés dans la restauration de peintures murales et ne se sont pas éloignées radicalement mais seulement marginalement de la méthodologie en usage. Dans cette intervention a eu une particulière importance l'emploi du mélange absorbant de cellulose avec de l'eau additionnée de carbonate d'ammonium (communément utilisé dans les phases de nettoyage) pour amollir la peinture à huile et permettre ainsi l'adhésion de la colle animale nécessaire pour l'entoilage et donc pour le strappo.

Les autres opérations habituelles ont été exécutées avec extraordinaire diligence et soin, vu le caractère exceptionnel et la grande délicatesse de ce travail.

METHODOLOGIE ET APPLICATION PRATIQUE DE LA SEPARATION D'UNE PEINTURE A HUILE SUR MUR D'UNE PEINTURE A FRESQUE SOUS-JACENTE

Cristina Danti
Inspecteur, historien d'art
Fabrizio Bandini, Guido Botticelli
Restaureurs
Opificio delle Pietre Dure e Laboratori di Restauro
Via degli Alfani, 78
50121 Florence, Italie

La découverte de deux ou de plusieurs peintures murales superposées est une chose fréquente; tout aussi fréquente est leur séparation par des opérations habituelles de dépose.

Utilisant désormais des méthodologies très expérimentées, ces opérations ne présentent normalement aucune difficulté particulière, et permettent de récupérer intégralement la peinture en surface ainsi que la peinture ou les peintures sous-jacentes. Il est bien connu que le procédé de dépose se base sur le fort pouvoir adhésif de la colle animale au niveau de la superficie peinte (que celle-ci soit exécutée à fresque ou à la détrempe).

Au cours de l'intervention de restauration (septembre 1985) sur quatre lunettes, peintes par Andrea Lilli dans le cloître de l'ancien couvent de Sant'Angelo Magno à Ascoli Piceno et représentant des épisodes de la vie de Saint Benoît nous avons rencontré un cas particulier pour lequel le principe énoncé ci-dessus ne pouvait conduire à aucun résultat si nous utilisions la méthodologie habituelle. Il a donc fallu individualiser et mettre au point quelques variantes à cette méthode, en cherchant pourtant de se maintenir le plus possible dans les limites de la pratique en usage (surtout en ce qui concerne le choix et l'utilisation des matériaux). Le cas anormal auquel nous faisons allusion, concerne la superficie à huile d'une des quatre peintures de Andrea Lilli, c'est-à-dire celle qui représente la "Naissance de Saint Benoît". Du reste les quatre peintures sont citées dans les anciens guides locaux comme peintes à l'huile; seulement dans le récent catalogue de l'exposition sur Andrea Lilli (AA.VV., "Andrea Lilli...", 1985, pp. 40-50), trois sont dites peintes à la détrempe et une, de façon incertaine, à huile, superposée "à une couche picturale précédente". Ce dernier point a été amplement confirmé par nos recherches, grâce auxquelles nous avons réussi, en outre, à certifier, pour les trois peintures, la technique d'application au Blanc de Chaux (la plus courante à cette époque et la plus conforme à un lieu extérieur), écartant donc définitivement d'autres hypothèses relatives à leur technique d'exécution.

Le cloître de Sant'Angelo, commencé par les Olivétains en 1463 et terminé seulement en 1517, était resté pendant des dizaines d'années sans aucune décoration picturale; dans le dernier quart du XVI^e siècle, un maître inconnu commençait à peindre sur le côté adjacent à l'église une grande scène représentant la "Naissance de Saint Benoît" mais la décoration ne fut pas poursuivie et ne fut reprise qu'autour de 1630 quand Andrea Lilli reçut la commande pour l'ensemble du cycle bénédictin. L'artiste, sans détruire la fresque préexistante, exécuta dessus, à huile, une nouvelle figuration de la naissance du Saint, se limitant à la lunette, pour continuer ensuite le cycle avec une technique plus commune.

Dans le catalogue cité ci-dessus, la lunette peinte à huile était jugée "désormais réduite à un état irréversible de dégradation": en effet, celle-ci avait subi dans le temps d'importantes pertes de pigment et, à l'examen visuel rapproché, à l'intérieur des lacunes nous pouvions observer la peinture à fresque sous-jacente. Nous avons donc poursuivi notre observation de la surface en utilisant la lumière rasante et des lampes à U.V.: de cette façon nous avons pu individualiser les traces des incisions qui marquaient les motifs architecturaux dans la peinture sous-jacente.

En outre, en exécutant des essais dans l'intonaco au-dessous de la lunette de Lilli, nous avons constaté que la fresque continuait aussi dans cette zone, bien que martelée pour y faire adhérer le nouvel intonaco.

A ce point, nous avons établi un accord avec la Surintendance aux Biens Artistiques et Historiques d'Urbino, pour récupérer la fresque cachée dans toute son intégrité; mais ceci évidemment signifiait la dépose de la peinture à huile qui couvrait le fresque au moyen d'une opération de strappo.

Nous avons commencé ainsi l'étude d'une méthode optimale pour conduire l'opération qui se présentait très difficile vu que la première couche semblait très compacte et adhérente à la superficie de la fresque.

Une série de petits essais ne donnèrent aucun résultat: en effet, la colle animale ne faisait pas prise sur la peinture à huile, tandis que, dans les lacunes, elle provoquait le strappo de la peinture à fresque. Des résultats semblables étaient obtenus par l'emploi du "Paraloid" à la place de la colle animale.

Le strappo de la peinture a été finalement effectué en septembre 1986.

Nous avons donc pourvu à l'amollissement de la peinture à huile et au dégraisage de la superficie, de façon à permettre à la colle utilisée pour le strappo d'adhérer fortement sur la peinture. Dans ce but, nous avons appliqué un mélange absorbant de cellulose et carbonate d'ammonium, l'enlevant dès qu'il commençait à sécher et procédant immédiatement à l'entoilage avec de la colle forte et une double couche de toile "calicot". Après 24 heures, nous avons constaté le séchage superficiel de la colle, tandis que l'intonaco et la peinture à fresque sous-jacents étaient encore humides. Avec la tension des toiles, la peinture à huile amollie et bien adhérente à l'entoilage a été détachée, laissant inaltérée la fresque qui apparaissait dans les lacunes et sur laquelle, étant encore humide, la colle n'avait pas encore fait prise. Le tout, une fois séparé du mur, a été déposé sur une surface plane, de façon à le laisser sécher lentement sans crêpissures. Quelques feuilles de pâte cellulosique nous ont permis d'aplanir la peinture aux endroits où elle avait tendance à gondoler.

Nous avons ensuite posé quelques poids sur ces feuilles pour assurer la régularité de la superficie pendant le séchage de la colle.

Puis sur le verso de la peinture à huile, nous avons étendu une couche de caséate de calcium et nous avons appliqué les toiles de support. Dès que cette structure eut fini de sécher, nous avons enlevé les toiles "calicot" de la superficie picturale, en faisant regonfler la colle avec des mélanges absorbants de cellulose et en la dispersant ensuite avec de l'eau chaude.

Dans sa situation actuelle, la peinture pourra être normalement remise sur un support d'usage courant, par exemple un support en résine polyester et fibre de verre.

Les nouveautés introduites dans la méthodologie habituelle, pour atteindre les buts que nous nous étions fixés, ont été principalement les suivantes:

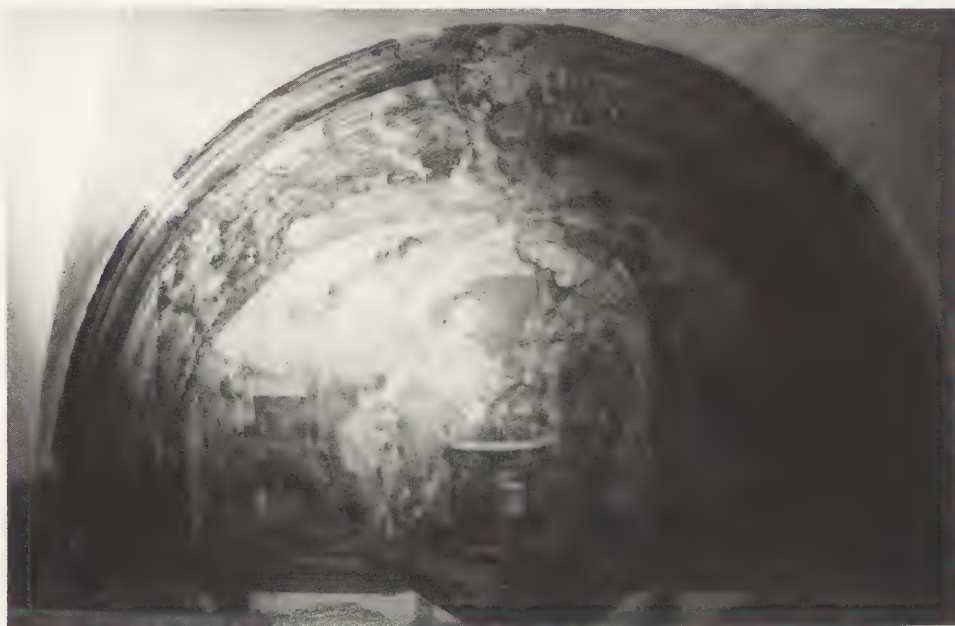
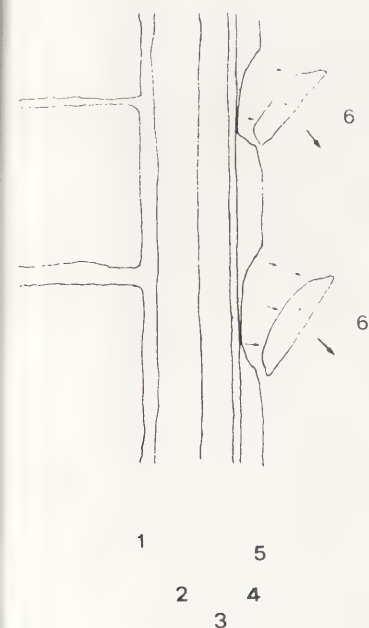
- A) exploiter la propriété du carbonate d'ammonium d'amollir, ou mieux de faire passer à l'état de "gel", les substances grasses (dans ce cas l'huile, le liant de la détrempe).
- B) exécuter l'opération du strappo en situation d'humidité, c'est-à-dire en opérant, pendant toutes les phases, avec l'intonaco encore mouillé pour éviter que la colle ne fasse prise sur l'intonaco lui-même (à fresque) mais seulement sur la peinture supérieure à l'huile (restituée à l'état de "gel" par le carbonate d'ammonium)

Il est évident que, pendant toutes les étapes du travail, nous avons observé au maximum toutes les règles relatives à l'opération de strappo.

En particulier:

- A) les deux toiles "calicot" ont été appliquées avec beaucoup de soin; elles ont été imprégnées uniformément de la colle et étendues manuellement dans tous les sens, évitant de provoquer des plis et des vides d'air entre peinture et toile. Les opérations d'entoilage ont été exécutées du bas vers le haut pour éviter que d'éventuelles coulées de colle ne compromettent la peinture.
- B) l'opération de strappo a été contrôlée attentivement; les toiles ont été maintenues toujours parallèles à l'intonaco jusqu'à la dépose complète et, ensuite, bien aplanies pour éviter des ondulations.
- C) l'utilisation du carbonate de calcium (insoluble dans l'eau), sur le verso de la peinture détachée, a été dans ce cas particulièrement précieux, comme un réel premier support à la peinture déposé.
- D) vu la délicatesse de l'intervention, dans le cas exposé ci-dessus, il nous semble utile de rappeler la méthodologie de la destitution des toiles en usage dans nos ateliers de restauration et appliquée sans variations: après avoir posé la peinture sur une table avec les toiles de protection vers l'opérateur, on étend de la pâte de bois (cellulose) humide, formant ainsi une fine couche; après un certain temps, quand la colle s'est imprégnée d'eau et bien regonflée, on étend sur la cellulose des sacs d'eau chaude pour faire regonfler encore la colle et pour qu'elle devienne fluide et transpire en grande partie à la superficie; après quoi on élève les sacs ainsi que la pâte de bois et avec soin les toiles et on disperse les résidus de colle toujours avec l'éponge et de l'eau chaude jusqu'à son élimination complète.

Grâce à cette intervention et malgré les grosses difficultés à surmonter, il a été possible de récupérer une peinture à fresque complète et encore en bon état, ainsi qu'une peinture à huile qui, laissée sur place, résultait fortement compromise dans sa lisibilité par la fresque sous-jacente qui apparaissait en superficie.

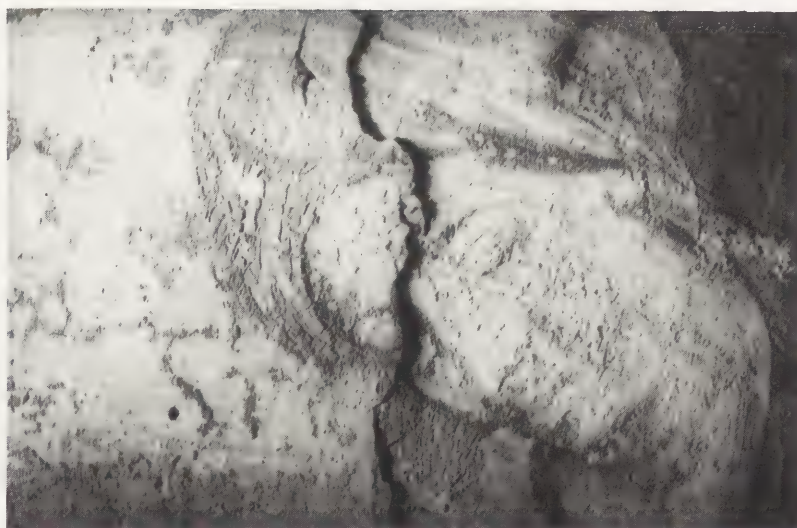


2) Andrea Lilli, peinture à huile sur mur représentant "La Naissance de Saint Benoît", ancien couvent de Sant'Angelo à Ascoli Piceno, avant la dépose.

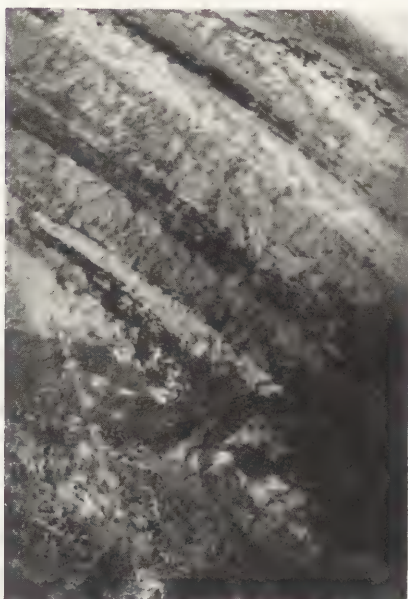
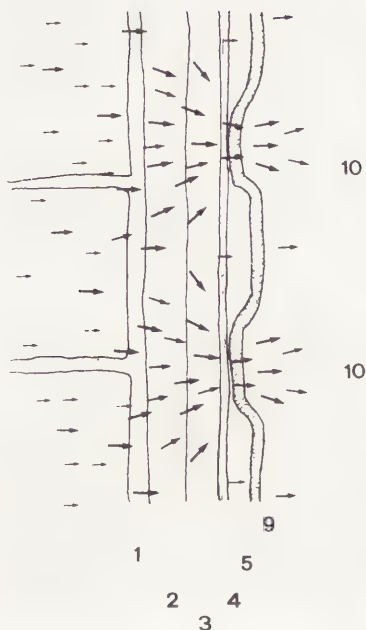
- 1)
1- Support mural
2- "Arriccio"
3- "intonaco" pictural
4- film pictural
5- peinture à la détrempe gras_{se}
6- perte du film



3) Detail de la figure 2.



4) Détail de la figure 2.



6) Detail de la figure 2.



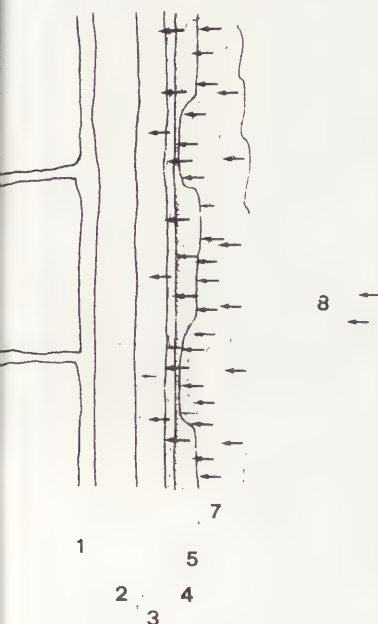
7) Phase du nettoyage: mélange absorbant de cellulose hydratée et carbonate d'ammonium.

5)

- 1- support mural
- 2- "ariccio"
- 3- "intonaco" pictural
- 4- film pictural
- 5- peinture à la détrempe grasse
- 9- entoilage de colle forte double toile de calicot et chanvre
- 10- l'humidité de l'intérieur du mur trouve meilleure voie de sortie à travers la superficie privée de pigment et en laissant ces parties humides et ne faisant pas consolider la colle qui au contraire séchait avec plus grande facilité sur la superficie intacte.



8) Phase de nettoyage: enlèvement du mélange absorbant.



9)

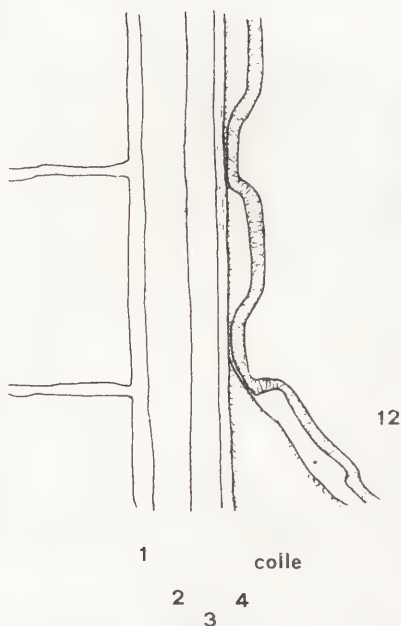
- 1- support mural
- 2- "arriccio"
- 3- "intonaco" pictural
- 4- film pictural
- 5- peinture à la détrempe grasse
- 7- le mélange absorbant de carbonate d'ammonium
- 8- l'humidité en pénétrant à l'intérieur du support pictural et à l'intérieur des couches sous-jacentes a agi en affaiblissant la peinture à la détrempe au niveau du film pictural à fresque.



10) phase du "strappo": application des toiles de calicot.



11) phase du "strappo": application des toiles de chanvre.



12)

- 1- support mural
- 2- "arriccio"
- 3- "intonaco" pictural
- 4- film pictural
- 12- le "stacco" de la peinture est advenu quand la colle, ayant déjà adhéré au film pictural (détrempe grasse), a réussi à transporter avec elle la matière en libérant complètement la superficie de la fresque.



13) Phase du "strappo": la dépose.



14) Phase du "strappo": la dépose.



15) La peinture, déposée, est en roulée .



17) Anonyme de la fin du XVI^e siècle, peinture à fresque représentant "La Naissance de Saint Benoît", réapparue sous la peinture à huile du même sujet.



16) La peinture, déposée, est fixée au verso avec du caséate de calcium .



18) Nettoyage de la peinture à fresque avec de la vapeur.

Bibliographie

"I^a Mostra di Affreschi Staccati", catalogo, Firenze, 1957

U. Procacci, "Sinopie e Affreschi", Milano, 1961

P. Mora - P. Philippot, "Technique et Conservation des Peintures Murales", Roma, 1965

E. Ferroni - D. Dini, "Su alcune esperienze orientative atte a favorire lo strappo o il distacco di affreschi inquinati da sali e affluorescenze". in "Bollettino CIHA", Aprile-Settembre, 1967

"Firenze Restaura", guida alla mostra, Firenze, 1972

G. Torraca, "Dipinti Murali", in Problemi di Conservazione", Bologna, 1973

P. Mora - P. Philippot, "La Conservation des peintures murales", Bologna, 1977

G. Torraca, "Dipinti Murali", in "Problemi di Conservazione", Bologna, 1973.

"Atti del Convegno sul Restauro delle Opere d'Arte - Firenze, 2-7 novembre 1976", Firenze, 1981

"Metodo e Scienza, operatività e ricerca nel restauro", catalogo della mostra, Firenze, 1982

"Andrea Lilli nella pittura delle Marche tra Cinquecento e Seicento", catalogo della mostra, Roma, 1985

F. Bandini, G. Botticelli, C. Danti, "Tecniche sperimentali per lo strappo di una pittura murale a tempera grassa su un affresco preesistente" in "O.P.D.-Restauro", Firenze, 1986

"Corso triennale restauratori d'opere d'arte 1984-1986, testimonianze di una esperienza formativa", Ascoli Piceno, 1986

Dessins au trait: Andrea Crescioli

Documentation photographique: Sergio Cipriani e Guido Botticelli

Rédaction: Bianca Vicentini

SUMMARY

The exfoliation and transfer on to a new support of later paintings is an important task in the restoration of painting. Ordinarily, when cleaning the original painting, later paintings over it have to be destroyed. The elaborated technique of exfoliation makes it possible to separate and conserve artistically valuable overpaintings with the original painting fully revealed. In the past, works on exfoliating overpaintings succeeded only on icons. The author of the paper elaborated in 1978-1980 techniques of exfoliating oil overpaintings from the earlier wall painting in oil. The most important step in exfoliation is the selection of organic solvents. The solvents are to soften up the overpainting layer, and not to affect the lower one. The elaborated technique of exfoliation is as follows. A flannelette compress with a solvent is made on the area to be exfoliated so that it should not touch the painting layer and damage the painting. It is hermetically sealed with polyethylene film from outside. The upper painting layer and the varnish layer underneath are softened up by solvent vapours effect. After the compress has been removed, the overpainting layer must be sealed with polyethylene film by means of a fast drying synthetic glue. The film prevents the solvent from evaporating out of the painting layer. The overpainting layer, glued on to polyethylene film, is gradually separated from the lower painting layer with a scalpel. The exfoliated painting is mounted on a new base made of foam cellular plastic, and the polyethylene film and synthetic glue are removed.

TECHNIQUE OF EXFOLIATING LATER PAINTINGS FROM WALL PAINTINGS IN OIL

S.V.Filatov
 "Spetzprojectrestavratzia" Institute of "Restavratzia"
 Objedineniye
 3/4 Bauman Gorodok
 Moscow 105037
 USSR

The disclosure of a painting by the exfoliation technique is the separation of the upper, later, painting layer from the earlier one underneath, and the transfer of the separated painting layer on to a new base. The later painting, hiding the original one, is in some cases of an artistic or historic value, therefore, it must not be removed by an ordinary restoration technique. In such cases the only method possible is the exfoliation technique.

In the USSR restorers of monumental painting resorted to the exfoliation technique in the 1940s. The academician I.E.Grabar said in 1947 at the meeting of the USSR Academy of Sciences, convened to celebrate the thirtieth anniversary of the Great October Socialist Revolution that the task of taking off and conserving the upper layer of fresco painting had been assigned to restorers, and substantial results had already been achieved. "P.I.Yukin, who specialized mainly in fresco painting, has achieved an exceptional success not only in removing frescoes from walls, which had been done in Italy, but also in exfoliating frescoes of different centuries. He succeeded in removing a 17th century layer by separating it from the lower 16th century layer..." (I.E.Grabar, "On Old Russian Art", Moscow, 1966, p. 378). Today, unfortunately, it is impossible to determine what this 17th century painting was like, whether it was executed on the plaster, or the painting layer was right on top of the 16th century painting. Judging by the fact that I.E.Grabar calls the 17th century painting a fresco, it must have been on the plaster. The description of the technique employed by P.I.Yukin has not remained either. It is noteworthy nonetheless that the urgency of the task of exfoliating and conserving later overpaintings on fresco painting was evident at early stages of development of Soviet restoration.

The exfoliation of overpaintings has from time to time to be resorted to, when restoring easel painting. Such experiments were conducted in Italy, Greece and Poland. In the Soviet Union the exfoliation of paintings from easel painting began to be experimented on back in the 1920s. A certain measure of success was achieved when film-forming synthetic glues began to be used for exfoliation. Thus, in 1975-1977, the author of the paper, together with the chemist A.V.Ivanova (VNIIR) worked out an exfoliation technique based on the use of polyvinyl butiral (PVB) for this technique to be used when restoring icons.

The following task, which was assigned to the Painting Research and Restoration Department of the "Spetzprojectrestavratzia" Institute, was the development of a technique of exfoliating later overpaintings from fresco painting. At the present time we have worked out a method of exfoliating wall painting in oil from the earlier painting layer executed in the same technique.

First of all, it was necessary to test whether PVB was suitable for exfoliating overpaintings from fresco painting. Such an experiment was conducted in 1978 on the fresco painting in the Church of John the Theologian at the Makarov Cemetery, the Mordovian ASSR. In this church the original painting in oil dates back to the late 18th century, and the overpainting, executed also in oil, dates from 1880s. The exfoliation technique employed for the wall painting was identical to that elaborated by us for icons. The process was as follows. A small compress of flannelette, wetted with an organic solvent selected in advance, was made on the overpainting area. When the overpainting layer was softened up sufficiently, the compress was removed, and an alcoholic solution of PVB was spread on the overpainting area. In 15-20 minutes PVB formed on the surface a translucent film firmly linked with the overpainting area. The glued overpainting layer was separated with a scalpel from the lower layer up to the border of the layer to be exfoliated. Another compress was applied nearby, on the next area, and the entire process was repeated. Thus, by moving on the compress, a small

fragment of the overpainting (17 by 12 cm.) depicting the head of an apostol, was gradually exfoliated and then mounted on a new base. A water solution of polyvinyl alcohol (PVA) was used to glue the overpainting on.

As a result of the experiment it became clear that PVB and PVA materials are suitable for exfoliating overpaintings from fresco painting in oil and for their mounting on another base. However, work on a vertical plane or a dome creates additional problems. The PVB glue film, put on the overpainting layer, is not mechanically strong enough when exfoliating large areas of overpainting. These drawbacks were to be eliminated in future, and the process to be simplified, since work on the wall of the building is more difficult than on an icon in a laboratory.

Further experiments to develop the technique were conducted in 1980, in St. Catherine Church, Bolshaya Ordynka Street, Moscow. The original oil painting in the dome of the church on evangelical subjects dates back to the third quarter of the 18th century. The layer of the oil painting over it dates from the 1860s. This later painting depicts large half-length images of evangelists.

The development of the technique was made difficult by the fact that the original painting had in some spots sustained losses, and plaster insertions concealed by the later painting layer. It would have been hard to use the two techniques, - "strappo", and the exfoliation technique since doing so required different materials and treatments. Therefore, it was necessary to develop a universal technique allowing to separate a later painting layer simultaneously from the original painting where it remained, and from the plaster where the original painting was lost.

A technique of exfoliating the overpainting in oil was developed after some experiments on unimportant areas of the painting. A compress with an organic solvent is to be applied to the area to be exfoliated so that it should not touch the painting surface and damage the painting layer. The compress is sealed with polyethylene film on the outside. The film is fixed to the wall with a medical plaster band over the entire perimeter. It is necessary to make sure that there are no holes left for the solvent vapours to pass outside. The overpainting layer is softened up only by the solvent vapours. A solvent, or a mixture of several solvents must be made of only volatile components. The exposure of the compress and solvents are to be selected individually by experimenting, and depend on the peculiarities of the painting. The applied compress can be heated with an electric bulb in order to activate the effect of the vapours. After the upper painting layer has been sufficiently softened up by the solvent vapours, the compress is taken off and the painting layer is glued over with a weak 2% solution of PVB by means of a wide soft brush. Then a concentrated solution of PVB (8%) is applied with the brush and the wet surface is sealed with polyethylene film. This film is carefully rolled over with a roller so that no air bubbles should be left under it. The overpainting layer, thus glued to the polyethylene film, is cut under with a scalpel and separated gradually from the lower painting layer or plaster. It is most convenient to begin exfoliation from the lower part of the fragment and roll the painting layer to be separated on a cylinder. After the painting fragment has been fully exfoliated, it must be taken off the cylinder, put on a smooth surface face down, sealed with polyethylene film on top, and pressed down with a weight to prevent any deformation. The weight can be removed in two or three days.

Foam plastic blocks are used as a tough base to mount the painting. A thin canvas or glass fabric must be first glued on the two sides of the foam plastic to reinforce it by means of a water solution of polyvinyl alcohol (PVB). Then the face of the base must be primed. The priming is made of chalk and a PVA water solution. Before glueing the painting layer on the surface of the prepared base, it is necessary to apply to it PVA (of 10-12% concentration), then put the painting layer reverse side down, roll it over thoroughly with a roller, remove the excess of PVA and put a weight on top for several days. After the glue has dried up, the polyethylene film can be removed from the surface of the painting layer. It is easily separated, helped on with a scalpel. A glue PVB film remains on the surface of the painting layer. It is removed with cotton tampons moistened in ethyl alcohol.

The developed technique was tested by the author of the paper in St. Catherine Church, B.Ordynka Street, in the dome on a fragment of the 19th century painting depicting the head of the

evangelist Mark. A 70 by 65 cm. area of the overpainting was exfoliated at one go. The lower part of the image was painted on top of an original painting in oil of the 18th century, and the upper part, on a plaster insertion. The compress exposure was four hours long. The exfoliation of the overpainting took three hours.

Essential points in this exfoliation technique are the use of solvent vapours to soften up the painting layer, and of polyethylene film as preventive sealing. The effect of solvent vapours excludes a risk of damaging the painting. The compress exposure can be from 2 to 15-17 hours, i.e., the compress can be applied in the evening, and the exfoliation can begin on the following day. Solvent vapours act more slowly, but much more effectively, since different paints of the overpainting are softened up evenly. The polyethylene film sealing not only reinforces the painting layer, but also impedes the evaporation of the solvent from it, therefore, the plasticity and pliability of the overpainting under the film remain for over twenty-four hours. Owing to this it is possible to exfoliate large fragments of the overpainting without concern that the softened painting layer will dry up again.

When employing this technique, it is necessary to select solvents carefully, so that they should soften up the upper painting layer and not affect the lower one.

The developed exfoliation technique has already been mastered by the restorers of the "Rosrestavratzia" Objedinenije. The technique can be used both to exfoliate oil overpaintings from an earlier painting in oil, and to remove the painting from a plaster base.

References

1. Grabar I.E. Nouvelles méthodes appliquées à l'étude des oeuvres d'art. - Mouséion, Paris, 1930, No. 11, p. 117.
2. Olsoufieff U.A. Problèmes de restauration des icônes et fresques. - Mouséion, Paris, 1934, No. III-IV, v. 27-28, p. 228-236.
3. Margaritoff T. Removing successive layers of painting: further work. - Conservation and Restoration of pictorial Art. London-Boston, 1976, p. 126-128.
4. Bilecki T., Kamiński J. Zdejmowanie przemiałowan obejnych z obrazów temperowych i osadzaniu na nowym podłożu. - Ochrona zabytków, 1978, No. 3, p. 182-190.
5. Филатов С.В., Иванова А.В. Метод отслоения записей с применением поливинилбутирала. - Художественное наследие, № 5, М., 1979, с. 122-125.
6. Лелекова О.В., Иванова А.В. Разработка методики отслоения записей станковой темперной и монументальной живописи. - Художественное наследие, № 7, М., 1981, с. 150-165.
7. Филатов С.В. Отслоение настенной масляной живописи. - Художественное наследие, № 9, М., 1984, с. 51-54.



RESUME

Les fragments de pigments bruts romains découverts à Baláca /Hongrie d'Ouest/ présentent une grande importance dans l'étude des pigments utilisés par les romains en Pannonia, ancienne Province de l'Empire romain. Ces fragments sont les seuls pigments bruts découverts jusqu'à maintenant sur le territoire hongrois actuel de Pannonia.

L'étude morphologique des fragments a fourni des informations intéressantes sur le mode de fabrication des pigments.

L'identification des matériaux a montré qu'on a utilisé aussi bien des pigments importés /bleu égyptien, appianum/ que locaux /dolomite, terre noire/.

L'ANALYSE DES PIGMENTS BRUTS ROMAINS DÉCOUVERTS A BALÁCA

Márta Járó

Chimiste

Direction Centrale de Musées

Budapest 100, P.O.B. 54, 1476 Hongrie

László Kriston

Physicien

Institut de Criminologie

Budapest, Maros u. 6/a, 1028 Hongrie

1. Introduction

Les fouilles effectuées à Baláca /Hongrie d'Ouest/ avaient mis au jour une des plus grandes et riches villas de Pannonia, ancienne province de l'Empire romain. La villa a été construite vers la fin du I^{er} siècle /1/. Les travaux de fouille ont été commencés au début de ce siècle, alors que des fragments de pigments bruts étaient découverts et déposés en réserve au musée municipal.

Les fragments: deux petites boules blanches, trois boules bleues /l'une d'eux double/, une boule cassée, une boule noire déformée et un fragment vert de forme irrégulière sont exposés actuellement au musée du site /Figure 1/.

Dans l'étude des pigments utilisés par les romains en Pannonia /2/ ces fragments présentent une grande importance, car ce sont les seuls pigments bruts découverts jusqu'à maintenant sur le territoire hongrois actuel de l'ancienne province Pannonia.

2. Analyse des pigments

C'est la diffraction des rayons X qui a été utilisée pour l'analyse des pigments, méthode permettant d'identifier des composés chimiques cristallisés. Pour compléter nos investigations la microscopie optique a été utilisée aussi dans certains cas.

2.1. Analyse par diffraction des rayons X: mode opératoire

L'analyse des pigments blancs et bleus a été effectuée par diffractométrie /appareil Siemens, Cu K α radiation, Ni filtre, 30 kV, 40 mA/. Les microprélèvements des pigments brun, noir et vert ont été irradiés dans une chambre Debye-Sherrer /diamètre: 114,6 mm, Cu K α radiation, Ni filtre, 40 kV, 60 mA, durée d'irradiation: 3 heures/.

2.2. Résultats

2.2.1. Pigments blancs

On a pu identifier dans les deux prélèvements la dolomite, la calcite, un peu de α -quartz et de feldspaths. L'examen au microscope montre que de la calcite cristallisée et recristallisée est également présente dans les échantillons. Il s'agit donc de dolomite contenant de la calcite mélangée avec de la chaux. S. Augustin mentionne que parmi les pigments blancs provenant de Pompéi il en existait notamment un en forme de boule de diamètre de 100 mm environ avec la marque du marchand /3/. Le diamètre des boules blanches de Baláca ne dépasse pas 20 mm et on ne trouve pas de marque sur la surface. D'après les résultats d'analyse publiés dans la littérature spécialisée étudiée par nous la dolomite n'était pas utilisée au centre de l'Empire. On ne l'a identifiée que dans les prélèvements pris des peintures murales de l'ancienne province Lydia /aujourd'hui la Turquie/ et à Lauriacum /aujourd'hui Enns, Autriche/ /4,5/. En Pannonia c'était un pigment très connu, vendu certainement comme une sorte de craie. On l'a utilisé non seulement comme pigment blanc /6/ mais aussi comme poudre blanche remplaçant la poudre de marbre dans la couche de préparation des peintures /7/.

2.2.2. Pigments bleus

La matière des boules bleues est composée de cristaux de silicate de calcium et cuivre, de α -quartz et d'un produit pas encore identifié mais présent dans tous les pigments bleus romains analysés par nous jusqu'à maintenant. Il s'agit donc du bleu égyptien, pigment bleu utilisé partout dans l'Empire. Les boules de diamètre de 10-15 mm ressemblent à celles mises dans le commerce à Pompéi /8/.

2.2.3. Pigment vert

L'analyse du fragment vert clair, pareil à la cire au toucher montre qu'il s'agit de glauconie très pure. La terre verte,



Figure 1: Les pigments bruts

couleur minérale de nature argileuse contient toujours des impuretés / α -quartz, silicates, carbonates etc./. Dans le cas de notre fragment, le manque de ces impuretés indique que la terre verte a été bien lavée et purifiée. Plinius parle d'un pigment vert, de l'appianum qui était préparé à partir de la craie verte et utilisé pour la falsification de la chrysocolla /9/. On peut supposer que le fragment analysé est l'appianum.

2.2.4. Pigment noir

La boule noire de diamètre de 20-25 mm environ se compose de α -quartz /l'élément majeur/, de muscovite/illite et de feldspath. L'examen au microscope montre que la matière terreuse ne contient pas les particules amorphes du charbon /constituant principal des pigments noirs romains/. Il s'agit d'une sorte de terre noire dont la couleur vient des matériaux organiques qu'elle contient.

2.2.5. Pigment brun

Les résultats de l'analyse montrent que la composition minéralogique de la matière de la boule brune est semblable à celle de la boule noire, mais pour obtenir la couleur brunâtre on a "dilué" la terre noire par de la chaux.

3. Conclusion

L'analyse des pigments bruts de Baláca nous ont fourni des données intéressantes à l'étude des matériaux utilisés par les romains pour l'exécution des peintures murales à Pannonia. La forme de boule des fragments /à part le fragment vert/ montre qu'ils proviennent du commerce.

Les boules noire et brune ont certainement la même provenance; leur forme de boule déformée montre qu'on les a faites à la main.

La forme sphérique parfaite et le même diamètre de deux boules blanches nous laisse penser à un mode de fabrication en gros, mécanisé.

La préparation du bleu égyptien et de l'appianum suppose une technique de fabrication de haut niveau.

Sur le territoire de Pannonia il y a plusieurs mines de dolomite et de gisements de glauconie. On peut supposer aussi bien l'existence d'une ou plusieurs manufactures de pigments /bien qu'on n'en ait pas encore découvert/ qu'une importation organisée. A notre avis les peintres de Pannonia ont utilisé aussi bien des pigments importés que locaux. Il pouvait exister des manufactures pour la production des pigments dont l'importation n'était pas économique /on en a utilisé une grande quantité/. En ce qui concerne les pigments comme le bleu égyptien ou l'appianum, l'importation devait être moins chère que la fabrication.

Remerciements

Les auteurs remercient Madame Edit Thomas, archéologue, membre de l'Académie de Science de l'Autriche, qui a attiré l'attention aux pigments bruts de Baláca et Madame Sylvia Palágy, archéologue, chef de département au Musée Bakonyi à Veszprém, qui a donné la permission à l'analyse.

Bibliographie

1. B. Thomas E.: Baláca, Akadémiai Nyomda, Budapest, 1964, pp.53.
2. Járó M.: Pannóniai falfestmények jellemzése spektrokémiai és röntgendiffrakciós módszerekkel /La caractérisation des peintures murales de Pannonia par des méthodes spectrochimique et diffraction des rayons X/, thèse de doctorat, Budapest, 1985, pp.95.
3. Augusti, S.: I colori pompeiani, De Luca Editore, Roma, 1967, p.52.
4. Eibner, A.: Entwicklung und Werkstoffe der Wandmalerei von Altertum bis zur Neuzeit, Verlag B. Heller, München, 1926. pp. 233-256.
5. Kottulinsky, L.: Bericht über die Restaurierung eines römischen Freskos, Arbeitsblätter, Heft 2/1981, pp.91-92.
6. Járó M.: thèse de doctorat, voir /2/
7. Járó M.: Preparation of wall paintings in the Roman province of Pannonia, according to recent investigations, Actes du 5^e Cours International pour Restaurateurs, 1.Vol., Veszprém, 1985, pp.83-88.
8. Augusti, S.: op. cit. p.63.
9. Augusti, S.: op. cit. p.101.

SUMMARY

The task involved the reconstruction of parts of a contemporary wall-painting in a late 18th c. pharmacy. Owing to the cracking of the vault the painting had to be removed from the wall. Separation was carried out with the help of a two-ply canvas glued by size.

Following the reinforcement of the vault and the renovation of the building the premises were turned into a medicinal herb store where the restored secco had to be reinstalled. The reverse side of the painting removed from the vault was evened out by lime mortar to which polyvinyl acetate was added. The stability of the pieces during the treatment to come was ensured by a layer of glass-cloth impregnated by epoxy synthetic resin. A rigid, pre-stressed, curved, railed aluminium support was stuck onto the assembled and completed secco. Firmness of the support was brought about by the tight jointing of the units in the compressed sector and stretcher cross-pieces in the drawn sector. The glass-cloth impregnated by epoxy resin stuck to the smooth reverse side of the secco as well as the aluminium grid fixed by glass-cloth and epoxy synthetic resin provided perfect firmness. The finished construction was attached to the wall by aluminium strap and wedges so that it was to some extent sunk into the vault.

The fragmentary nature of the restored painting as well as the reconstruction of the contemporary painting of the vault around the secco was made discernible by applying a different hue for retouch and the reconstructed parts, by retaining the uneven edges of the latter as well as making it protrude from the wall-face.

THE APPLICATION OF A PRE-STRESSED, CURVED, RIGID SUPPORT IN THE RESTORATION OF AN 18th c. SECCO PAINTED ON A WAGON VAULT

András Morgós

Chemical engineer, restorer

National Centre of Museums, Restoration Department

H-1087 Budapest, Könyves Kálmán krt. 40

József Lőcsei

Chemical engineer, restorer

Hajdusági Múzeum

H-4220 Hajduböszörmény, Kossuth u.

1. Introduction

The rehabilitation of historic town centres in Hungary has been going on for almost two decades now. In order to meet the complex requirements of the protection of monuments, architectural reconstruction is preceded by research in art history. The wall-painting referred to above was discovered on the wagon-vaulted ceiling in the ground-floor room of an 18th c., late Baroque building erected on mediaeval foundations and situated in the historic town centre of Győr. The painting made by the "secco" technique has no special artistic value, but is a true reflection of the state of decorative art in a small 18th century country town, therefore the National Inspectorate for the Protection of Monuments decided to have it renovated. The painting decorated the walls of a contemporary pharmacy. The walls were painted black with yellow stars on it and with a medallion in the middle field of the ceiling. The paintwork has greatly deteriorated as a result of the successive conversions of the building, so reconstruction was confined to one medallion and a few pieces of plaster with the starry pattern on them.

Owing to the static conditions of the cracked arched ceiling, the painting had to be removed from the vault. Restoration of the full wall-surface did not seem feasible. The aim was, therefore, to present the contemporary state of the premises by anastylosis of the restored fragments as well as their partial reconstruction.

The fragmentary character of the contemporary painting of the ceiling - including the medallion - was made discernible by using a different hue for the retouch of the original details and for the painting of the reconstructed parts as well as retaining the unevenness of the edges and by making it protrude from the wall-face.

2. Restoration

2.1. In the first phase of the work the painted surfaces were uncovered. In some places there were as many 20 layers of whitening used for repainting. After fixing /Paraloid B72/ and cleaning the surface two layers of canvas were stuck by size onto the painting to be removed. Following this the plaster was removed from the ceiling. The rough coating whose thickness varied between 2-20 mm was made of extremely hard lime-mortar with small-sized gravel. Due to the electric cables passing through the painting was removed in five pieces. The detached fragments were laid on a centre arch /templet/ the curvature of which was identical with that of the vault. After having filed away the reverse side, a one-centimetre intervention layer of lime mortar reinforced by an acetate dispersion was formed. This layer - in between the paintwork and the support - makes it possible for us to remove the painting again in case it should seem necessary at any future time. After having applied the lime mortar onto the pieces, TIPOX IHS^x epoxy resin was used to stick the glass-cloth to them. That is how the appropriate curvature and the required solidity was attained for the rest of the treatment. After the resin had set, the pieces were turned over, the canvas stuck onto them was removed by water, following which the pieces were assembled and the lacunae completed. The next step was the making of a support. When devising it, one had to consider the following requirements:

- it must provide firm support for a paintwork of 3 m²;
- the fixing of the restored unit with a total weight of 75 kilos on the ceiling should be simple;
- it must provide the required curvature without any distortion;
- it must be completely rigid,
- it should be considerably shock-resistant so that it could

^x epoxy adhesive resin produced by Tiszai Vegyikombinát, Leninváros, Hungary

resist various effects during transportation and fitting;
- its thickness should not surpass 40 mm.

2.2. First the longitudinal beams of the support frame were prepared from L-section aluminium units which were riveted to each other. These were placed at a distance of 150-200 mm along the longitudinal section of the painting. Its ends reached beyond the edges of the painting by about 200 mm. The longitudinal beams were joined by T-section units so that the support units should fit tightly in both directions. This is necessary so that the pressing force which originates from weight - and is to be reckoned with when there is any curved structure involved - should not be born by the rivets only.

In suspended, curved structures stretching forces arise above the centre line along the transversal section. These forces arising in the so-called drawn field have been compensated by transversal aluminium cross-pieces. Thus we prevented that the edges of the finished painting should bend inwards. Aluminium rods of 6 mm in diameter were fitted into the compartments of the support to make a grid.

The aluminium frame thus prepared was placed on the reverse side of the painting. Glass-cloth was laid into the compartments and was stuck to the epoxy synthetic resinous glass-cloth on the reverse side of the painting by epoxy resin in order to fix the support on the secco. After the setting of the resin the construction was perfectly rigid. The painting mounted on the support was then retouched using earth colours bound by an acetate dispersion.

The pieces of plaster with the starry pattern on them were reconstructed in a similar manner. Here, however, owing to the small surface involved one epoxy - glass cloth layer was sufficient.

3. Replacement of the secco

After the reconstruction of the building had been finished the wall-paintings were taken back to the location. A 15 mm deep nest was prepared in the vault and the restored unit was attached to the arch by screwed wedges and aluminium straps. Following the load tests /+150 kilos of extra weight per strap /the starry plaster pieces were also attached to the arch and embedded in mortar; thus the final shape of the arched ceiling was obtained. The arched field protrudes by about 20 mm from its environment and its edges have been pared off in a slanting direction. A gap of about 10 mm was left in between the fitted painting and the walling of the vaulted nest in order to compensate for the coldness radiating from the wall behind; in this manner the condensation of humidity on the painting can be prevented.

In order to protect it from the settling of various microorganisms it was brushed over by 1% pentachlorophenol in alcohol.



Fig. 1. The medallion with the double-eagle while uncovering

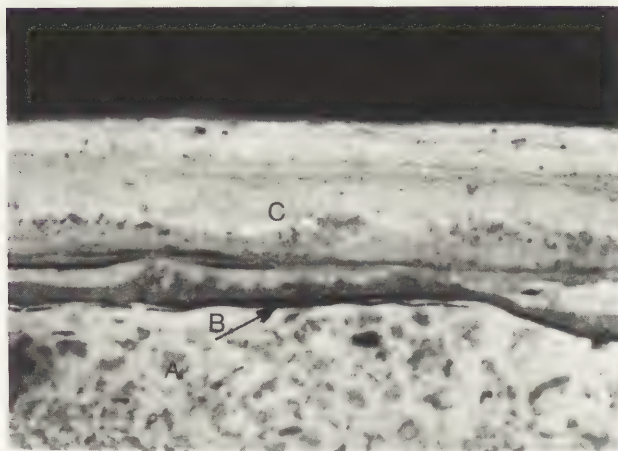


Fig. 2. A microscopic photograph of the plaster sample in the environment of the wall-painting
 A - plaster
 B - original paint layer
 C - subsequent whitewashes

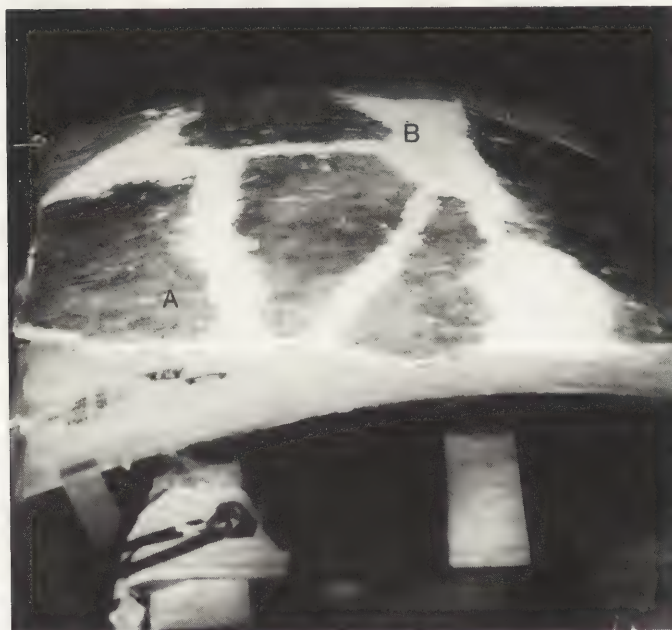


Fig. 3. The reverse side of the medallion assembled on the centre arch /templet/ A - A fragment of the painting with the first reinforcing synthetic resin - glass cloth layer
 B - completions

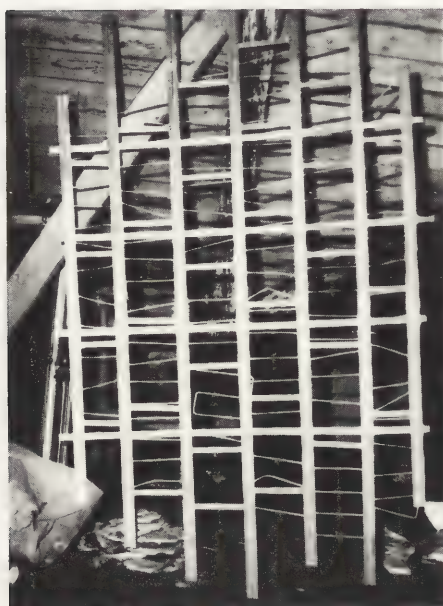


Fig. 4. The finished curved aluminium support

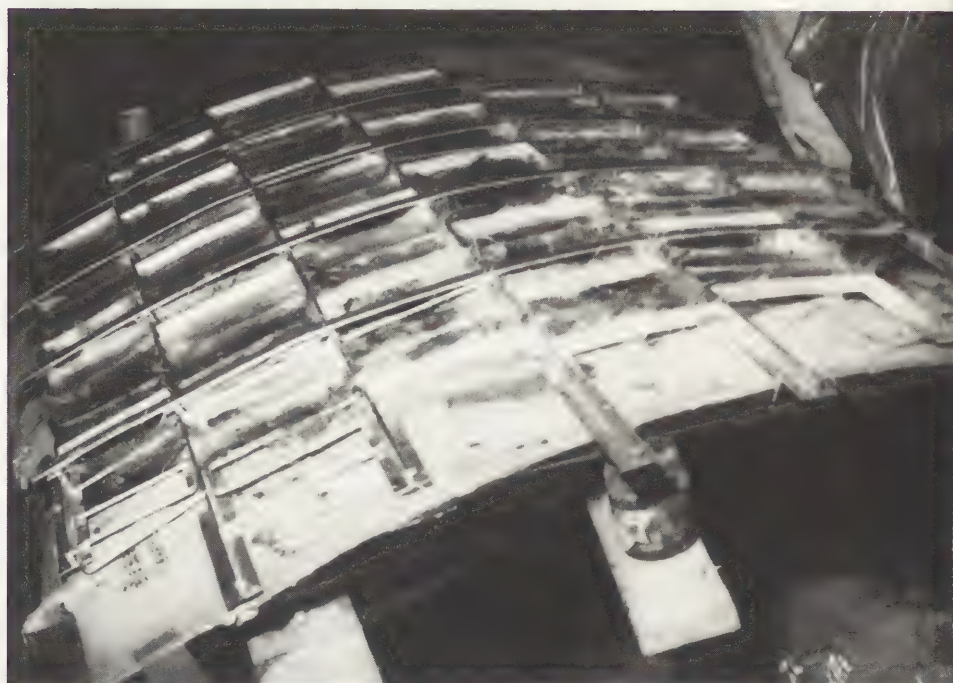


Fig. 5. The support stuck on the painting

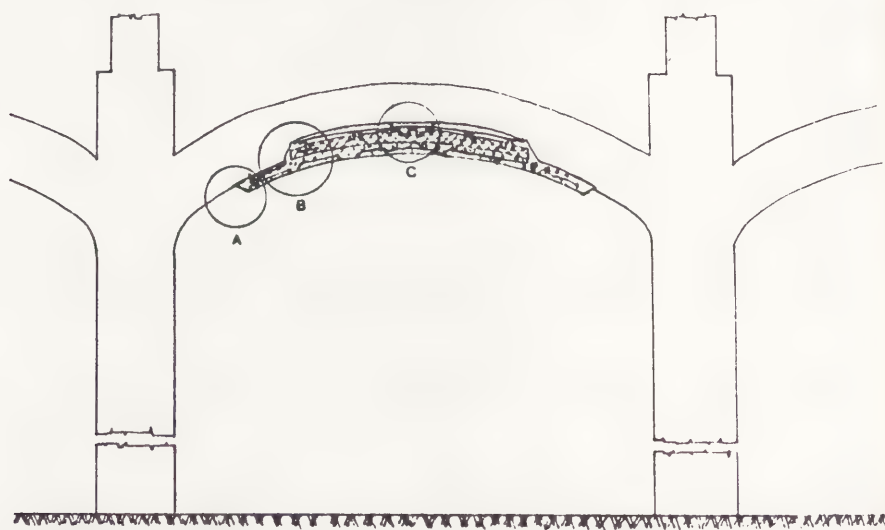


Fig. 6. The secco reinstalled onto the vault

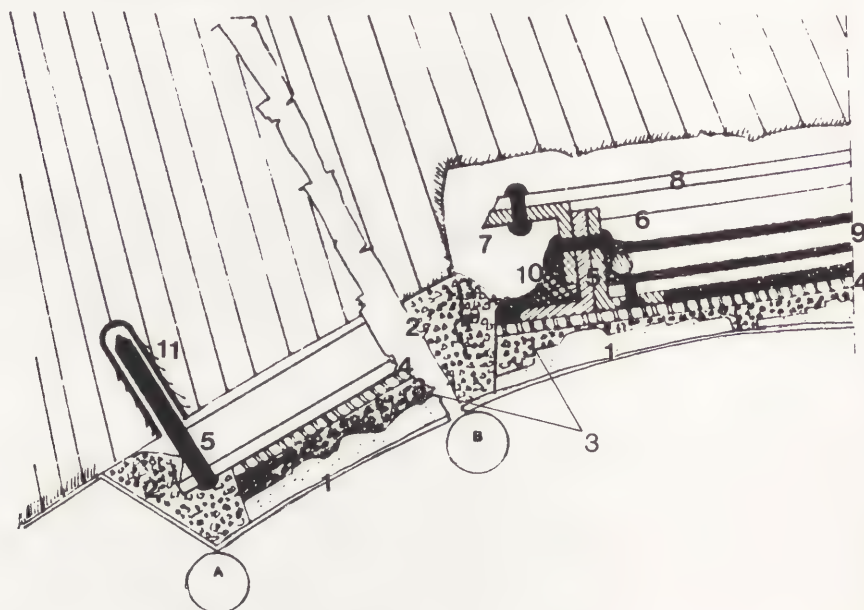


Fig. 7. The pattern of Sections A and B for Fig. 6.

- 1 - original plaster
- 2 - mortar in which the pieces of the painting reinstalled onto the vault were embedded
- 3 - mortar containing acetate dispersion used to even out the reverse side of the detached painting
- 4 - epoxy resin + glass-cloth layer
- 5, 6, 7, 8, 9 - parts of the support unit
- 10 - epoxy resin + glass cloth applied to join the support and the painting
- 11 - screw wedges fixing the original painted fragments to the ceiling

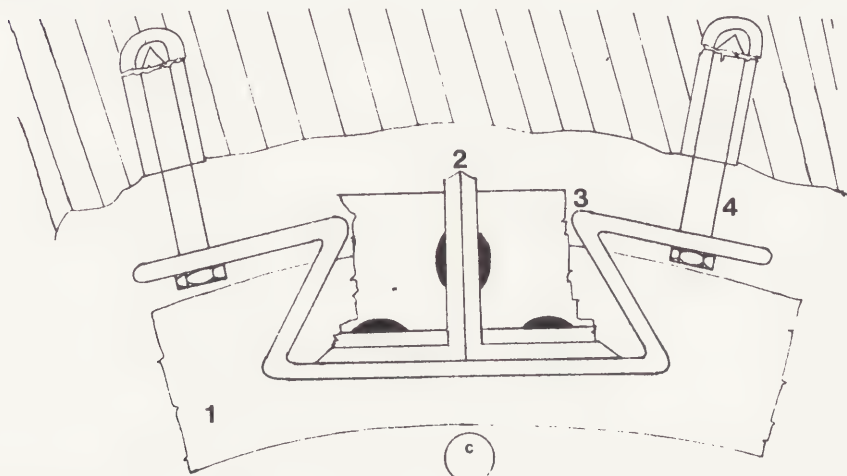


Fig. 8. Aluminium strap fixing the support to the ceiling

- 1 - the mounted painting
- 2 - the longitudinal support unit reaching beyond the edges of the painting
- 3 - suspension unit /aluminium strap/
- 4 - screw wedges fixing the aluminium strap to the ceiling

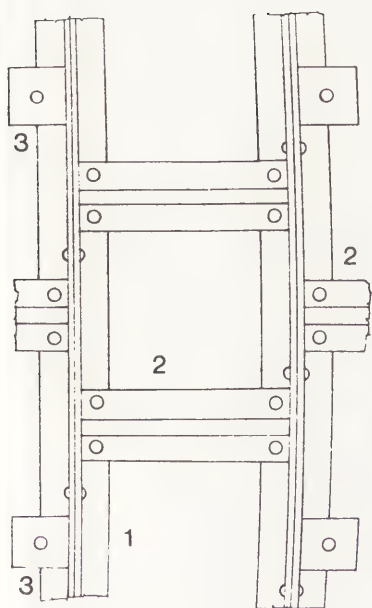


Fig. 9. Plan of the grids of the support unit

- 1 - longitudinal support unit
- 2 - transversal support unit
- 3 - the unit fixing the stretching aluminium straps



Fig. 10. Detail of the restored arched ceiling



RESUME

Dans le cadre des travaux de conservation de la fresque de Hans Erni au Musée d'Ethnographie de Neuchâtel, le Laboratoire de Conservation de la Pierre de l'E.P.F.L. a étudié la possibilité de consolider l'enduit de chaux dégradé au moyen d'esters siliciques.

Quatre produits commerciaux ont été testés. Leur efficacité a été vérifiée par des essais mécaniques, d'absorption d'eau et de dilatation hydraulique.

Afin de définir s'il était préférable de consolider l'enduit avant ou après l'application des couleurs, un essai simulant l'effet de l'eau de pluie, principal facteur de dégradation de l'oeuvre, a été réalisé.

Les résultats obtenus montrent que la consolidation d'un mortier de chaux, ayant une faible cohésion, est parfaitement réalisable avec les esters siliciques.

Le procédé, qui consiste à appliquer le consolidant en dernier, c'est-à-dire après l'application des couleurs, se révèle sans doute le meilleur.

CONSERVATION DE LA FRESQUE DE HANS ERNI
AU MUSEE D'ETHNOGRAPHIE DE NEUCHÂTEL - SUISSE
— ETUDES PRELIMINAIRES —

R.Pancella*, V.Furlan*, F.Girardet*, M.Stähli**

* Laboratoire de Conservation de la Pierre
de l'Ecole Polytechnique Fédérale de Lausanne
Chemin de Bellerive 32 - CH-1007 Lausanne

** Atelier de Restauration d'Art
Chemin des Lerins 41 - CH-2854 Auvernier

1. INTRODUCTION

La fresque de l'artiste suisse Hans Erni, au Musée d'Ethnographie de Neuchâtel, a été exécutée sur l'entière façade Nord du bâtiment, du 12 octobre au 3 décembre 1954.

Le thème développé, dans les 166.5 m² de surface, représente l'histoire de l'homme à travers les civilisations (fig. 1 et 2) et, comme le dit Jean Gabus, directeur du Musée à cette époque, "... C'est un bilan de la condition humaine, une page d'histoire qui reste ouverte sur le passé comme sur l'avenir, une page qui n'est pas close." /1/.



Figure 1 : Partie centrale de la fresque, état en 1954 après exécution.
(photo Musée d'Ethnographie de Neuchâtel)



Figure 2 : Partie inférieure de la fresque, état en 1954 après exécution.
(photo Musée d'Ethnographie de Neuchâtel)

Réalisée sans doute dans de mauvaises conditions climatiques -Gabus relate que : "... Il fait froid. C'est déjà une température de décembre avec un vent du Nord qui heurte la fresque de plein fouet ..." /2/- (fig. 3 et 4), cette oeuvre, exposée notamment à la pluie, a commencé à se dégrader après peu de temps et, en l'espace d'une trentaine d'années, toute la couleur avait déjà disparu. Pratiquement, seuls les traits de contour du dessin gravé dans l'enduit de chaux dégradé sont restés visibles.



Figure 3
Préparation d'une "journée de travail".
(photo Musée d'Ethnographie de Neuchâtel)

En 1981, l'Atelier de Restauration de Marc Stähli a été chargé par la Commission responsable de la conservation de l'oeuvre d'étudier les possibilités d'une éventuelle rénovation de la peinture. En fonction des observations effectuées sur la fresque par le restaurateur, un programme d'essais a été établi dans le but de vérifier si la consolidation de l'enduit était possible et d'établir le procédé d'application des couleurs qui donnerait la plus grande garantie de durabilité. Sur la base des investigations effectuées, la Commission a approuvé les propositions d'intervention du restaurateur, et l'artiste a accepté de participer lui-même à la rénovation de son oeuvre 28 ans après sa création. Mis à part alors les problèmes purement techniques, la conservation de l'oeuvre posait évidemment toute une série de questions éthiques et philosophiques /3/ :

*Dans quelle mesure l'oeuvre sera-t-elle complétée et rehaussée ?
Faut-il estimer que l'oeuvre d'art est un document historique
et que sa restauration et sa rénovation équivalent à une altération,
voire à une falsification ?
L'artiste n'a plus la mentalité de l'époque et son style a évolué :
reste-t-il le propriétaire de son oeuvre ?
Dans quelle mesure l'évolution matérielle de l'oeuvre sera-t-elle
influencée par l'apport de nouveaux éléments nécessaires à la
conservation de l'enduit et à sa rénovation ?*

Sans entrer dans des discussions d'éthique de la conservation, nous nous limitons, dans cet article, à relater les résultats des études qui ont précédé les travaux de rénovation.

2. HISTOIRE MATERIELLE DE L'OEUVRE

Dans la première phase de l'étude, on a essayé de réunir le maximum de renseignements sur l'exécution de la fresque et sur les présumées interventions postérieures. A cet effet, une documentation importante a été établie. Il en résulte que déjà en 1963 on se soucie de la dégradation précoce de l'oeuvre, et qu'en 1965 on se demande si la construction d'un avant-toit ne serait pas une première mesure de conservation.

En 1966, l'examen d'un échantillon de la fresque, effectué par l'Istituto Centrale del Restauro de Rome, révèle une très faible cohésion du mortier et une grande sensibilité à l'eau de la couche picturale. Dans la même année, une entreprise locale de plâtrerie-peinture réalise des imprégnations avec une dispersion et suggère de renouveler l'imprégnation tous les six à huit ans. On songe à remplacer la fresque par une mosaïque.

En 1970, l'application d'un produit acrylique est proposée par une autre entreprise du lieu. On exécute également un essai d'imprégnation avec un produit à base de silicone.

Il est à noter que pour toutes ces tentatives, l'emplacement des essais, le mode d'application et la dénomination exacte des produits ne sont pas indiqués.

Dans la deuxième phase de l'étude, un diagnostic précis sur l'état de conservation de l'oeuvre a été établi.

3. ETAT DE CONSERVATION EN 1981

La fresque est quasi totalement délavée, les pigments encore présents à la surface de l'enduit sont pulvérulents et ne résistent pas à la friction à sec d'une brosse douce et encore moins à l'eau (fig. 5a, 5b et 6). Seules les zones protégées par la partie supérieure du cadre en béton qui fait office de petit avant-toit et par la tablette de la fenêtre Ouest présentent encore quelques témoins résistants.

La surface de l'enduit montre encore une cohésion acceptable dans les premiers millimètres, mais la sous-couche est parfois très friable. Des soulèvements importants de l'enduit sont remarqués notamment à la limite des "journées de travail", et presque toujours où la surface a fortement été lissée à la truelle.



Figure 4
Report, par gravure, du dessin sur l'enduit.
(photo Musée d'Ethnographie de Neuchâtel)

Un réseau de microfissures (*fig. 7*), visibles au binoculaire et par lesquelles l'eau de pluie pénètre, est relevé sur toute la surface et surtout entre le sommier en béton et le mur en brique.

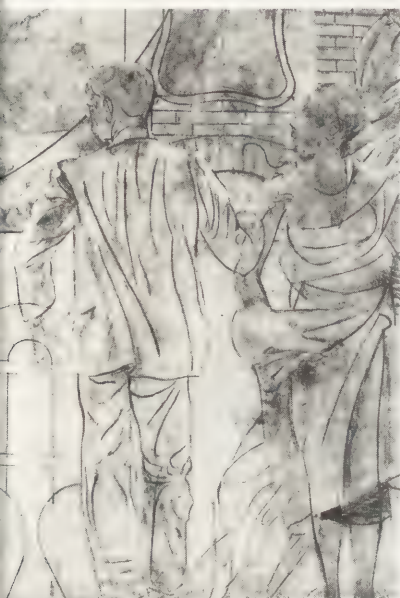


Figure 6
Détail de l'état de dégradation : on remarque la disparition quasi totale des couleurs et seuls les contours du dessin subsistent (comparer cette illustration avec celle de la figure 1, personnage en bas à droite).
(photo M. Stähli)

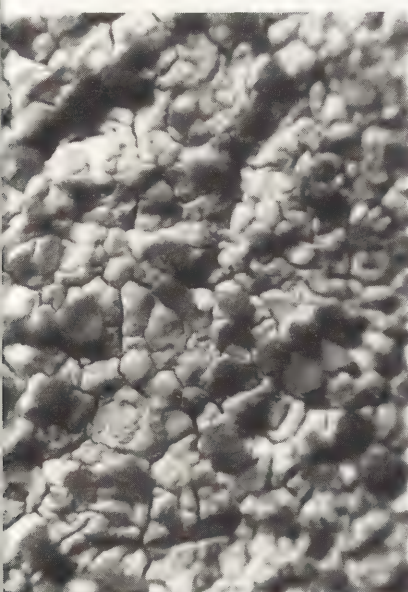


Figure 7
Macrophotographie des microfissures présentes à la surface de l'enduit.
(photo M. Stähli)

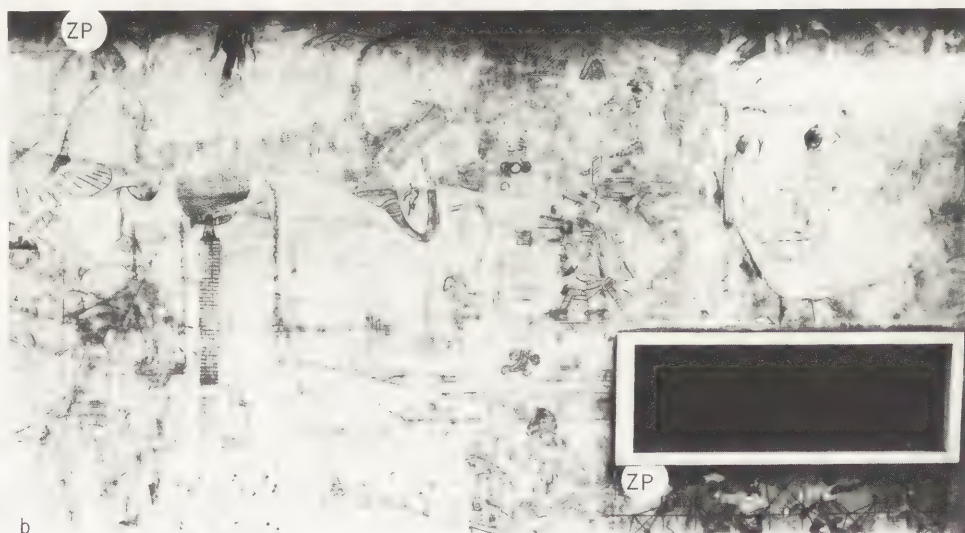
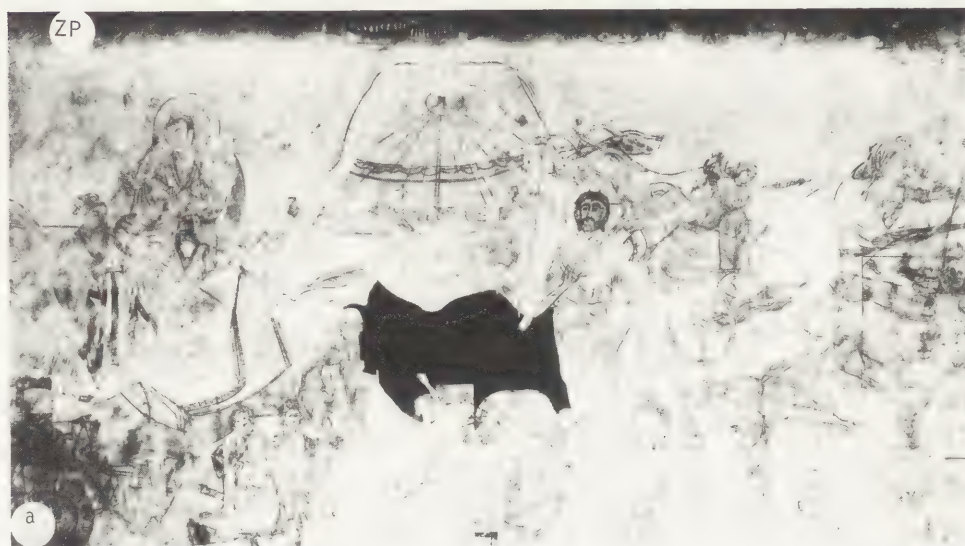


Figure 5 : Etat de la fresque en 1981 : disparition quasi totale de la couleur, à l'exception des zones protégées (ZP) par le petit avant-toit et par la tablette de la fenêtre Ouest.

a) Partie gauche, au milieu, en noir : essai d'application d'une peinture au silicate.

b) Partie droite.

(photo Musée d'Ethnographie de Neuchâtel)

En outre, les observations effectuées ont permis de mettre en évidence 31 journées de travail dont les surfaces varient de 2 à 10 m², de localiser 4 essais de fixage et 1 essai d'imprégnation fait avec un silicone, et de constater l'adhérence insuffisante de l'enduit au support à plusieurs endroits.

4. ETUDE EN LABORATOIRE

Sur la base des renseignements fournis par le restaurateur, notre laboratoire a étudié la possibilité de consolider l'enduit de la fresque avec des silicates d'éthyle, produits qui se révèlent très efficaces pour la pierre /4, 5/. Quatre produits commerciaux ont été testés. Leur efficacité a été vérifiée sur des éprouvettes de mortier à la chaux aux caractéristiques analogues à celles de l'enduit de la fresque.

Afin de répondre à la question s'il était préférable d'effectuer la consolidation de l'enduit avant ou après l'application des couleurs, un essai de durabilité, simulant l'effet de l'eau de pluie, a été réalisé sur des éprouvettes préparées selon les divers procédés envisagés par le restaurateur.

4.1. Préparation du mortier à la chaux

L'enduit de la fresque est caractérisé par une structure fine et une très faible cohésion : il s'effrite et se désagrège au toucher. Le sable est fin et pratiquement monogranulaire avec des grains dont le diamètre est inférieur à 0.5 mm (*fig. 8*). Compte tenu de ces caractéristiques, des éprouvettes 4x4x16 cm de mortier à la chaux ont été préparées en utilisant un sable de quartz de 0.5 mm et une chaux en pâte (chaux de fosse) éteinte depuis une année. Afin de reproduire un mortier ayant une faible résistance mécanique, le dosage en volume utilisé est d'environ 1:3; ceci correspond à un mélange d'environ 13 kg de sable sec et 3 kg de chaux en pâte. La mise en place a été faite par damage à la main.

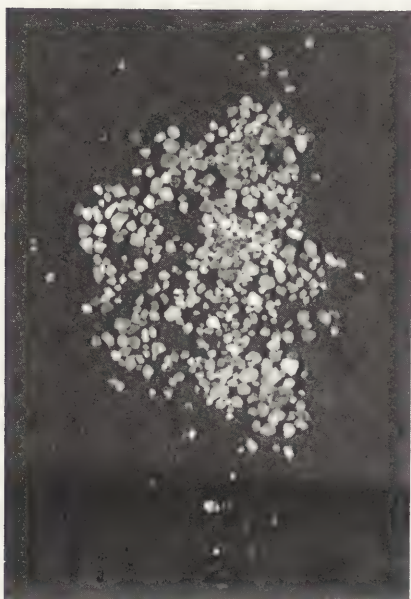


Figure 8
Séparation des grains de sable de l'enduit de chaux.
(photo B. Muhlethaler)

Après démoulage, les éprouvettes ont été carbonatées artificiellement avec du CO₂ afin d'accélérer le processus de durcissement et obtenir une carbonatation totale.

Dans les figures 10, 11, 12 et 13, sont comparés les caractéristiques physico-mécaniques du mortier témoin (T) et des mortiers traités (A, B, C et D).

4.2. Produits de consolidation et imprégnation des éprouvettes

Les produits pris en considération sont :

- A = Keimsilex
- B = Monumentique
- C = Wacker OH
- D = Motema 28

Ces produits sont tous à base de silicates organiques dissouts dans des solvants appropriés. Leur contenu en matière solide, après évaporation des solvants et hydrolyse pendant 42 jours à une température de 20°C et à une humidité relative de 50%, est reporté sur le tableau I.

produits	matière solide % en poids	matière volatile % en poids
Keimsilex	32	68
Monumentique	30	70
Wacker-OH	34	66
Motema 28 *	62	38

* après 42 jours, le Motema 28 demeure encore à l'état plus ou moins liquide

Tableau I
Contenu en matière
solide des
consolidants.

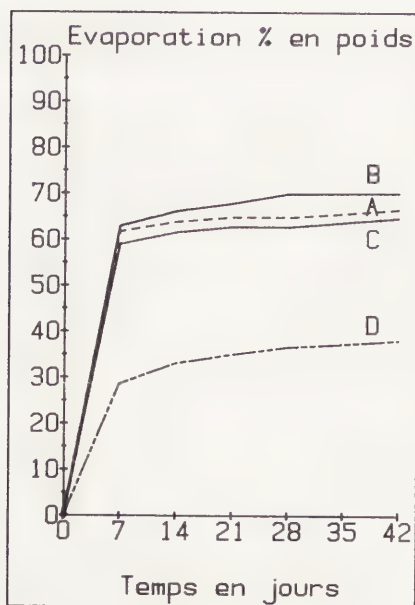


Figure 9
Evaporation des substances
volatiles dans les éprouvettes
de mortier traitées avec les
consolidants.

Les solutions de silicates organiques, méthyl ou éthylsilicates, à l'air, par évaporation, perdent le solvant puis, sous l'effet de l'humidité, s'hydrolysent selon la réaction suivante :



Les alcools libérés s'évaporent et l'acide silicique condense en gel de silice avec perte d'eau :



Le pouvoir liant est dû aux propriétés spécifiques de la silice amorphe qui, selon la nature des matériaux, peut également établir des liaisons chimiques.

L'imprégnation des éprouvettes de mortier a été faite par capillarité jusqu'à imbibition totale, et ceci afin d'obtenir des échantillons imprégnés de manière homogène. Le tableau II résume les données relatives à l'imprégnation; les valeurs reportées représentent la moyenne de 7 éprouvettes.

La figure 9 donne, en fonction du temps, l'évaporation des substances volatiles -solvants, radicaux alcooliques et eau- pour chaque série d'éprouvettes imprégnées. Il est à noter que la porosité très élevée du mortier favorise l'évaporation et que celle-ci a lieu pratiquement à la même vitesse que pour les produits purs. Comme on peut le constater, le départ de la matière volatile s'effectue en grande partie dans les premiers sept jours.

Le Keimsilex et le Wacker OH ont un comportement analogue. Le Monumentique présente une évaporation un peu plus rapide contrairement à celle, lente, du Motema 28 qui, après 42 jours, reste encore dans un état gélatineux (durcissement incomplet).

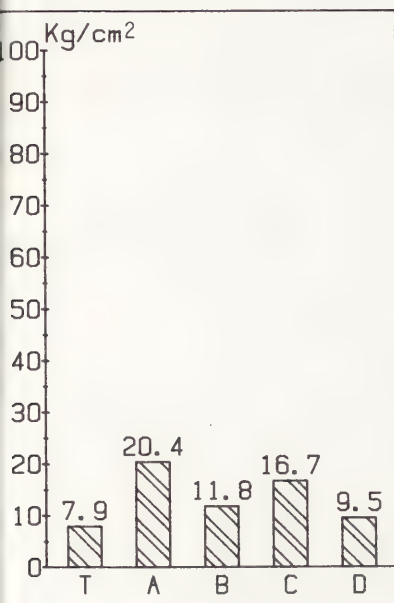


Figure 10
Eprouvettes consolidées :
résistance à la flexion.

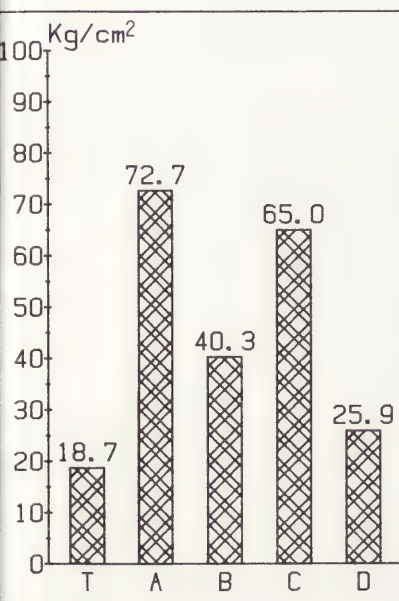


Figure 11
Eprouvettes consolidées :
résistance à la compression.

produits	P ₁ g	P ₂ g	P ₃ g	P ₂ - P ₁ g	ρ _p g/cm³	V _p cm³	V _e cm³	C.I. V _p /V _e	P ₃ - P ₁	matière liquide solide % du poids	
Keimsilex	479.1	526.2	495.0	47.1	0.96	49.1	50.3	0.98	15.9	9.9	3.3
Monumentique	486.9	532.8	500.5	45.9	0.97	47.3	51.2	0.93	13.6	9.4	2.8
Wacker-OH	474.6	523.3	491.9	48.7	0.94	51.8	49.9	1.04	17.3	10.3	3.7
Motema 28	483.5	533.4	514.6	49.9	0.96	51.9	50.8	1.02	31.1	10.3	6.4*

légende

P₁ = poids des éprouvettes après carbonatation et avant imprégnation
P₂ = poids des éprouvettes après imprégnation
P₃ = poids des éprouvettes après évaporation du solvant et hydrolyse pendant 42 jours
P₂-P₁ = quantité de produit liquide introduit dans le mortier
ρ_p = densité du produit liquide
V_p = volume du produit liquide introduit dans le mortier
V_e = volume des vides calculé en tenant compte de l'absorption d'eau à la pression atmosphérique (A)
V_e = $\frac{P_1 \cdot A}{\rho_r}$ où ρ_r = masse volumique réelle
C.I. = coefficient d'imprégnation = $\frac{V_p}{V_e}$
P₃-P₁ = quantité de matière solide dans le mortier
* = cette valeur comprend la matière active + une partie des produits non évaporés

Tableau II : Résultats de l'imprégnation : les valeurs représentent la moyenne de 7 éprouvettes.

4.3. Comportement mécanique

Les essais de flexion et de compression (fig. 10 et 11), effectués 42 jours après l'imprégnation, montrent que tous les produits ont un effet consolidant certain. Les meilleurs résultats sont donnés par le Keimsilex et le Wacker OH. Le premier confère au mortier une résistance supérieure d'environ 2.6 fois en flexion et 4 fois en compression. Le second donne des valeurs légèrement inférieures. Le Monumentique a un pouvoir consolidant plus faible tandis que dans le cas du Motema 28 l'augmentation de résistance est négligeable par le fait qu'après 42 jours l'évaporation et l'hydrolyse sont incomplètes.

4.4. Comportement à l'eau

Le comportement du mortier consolidé vis-à-vis de l'eau a été évalué par des essais d'absorption et de dilatation hydraulique /6, 7/ dont les résultats sont reportés respectivement sur les figures 12 et 13. Tous les produits réduisent initialement l'absorption d'eau. Toutefois, après 48 heures, les éprouvettes consolidées avec le Keimsilex et le Monumentique présentent la même absorption que les témoins. Le Wacker OH, bien que n'étant pas un hydrofuge, confère au mortier une certaine hydrophobie qui tend à disparaître avec le temps. L'hydrophobie marquée du Motema 28 est évidemment en relation avec le durcissement très lent du produit. La dilatation hydraulique linéaire est légèrement inférieure, par rapport aux témoins, pour toutes les éprouvettes traitées. Cependant, la comparaison des deux graphiques montre que la dilatation n'est pas proportionnelle à la quantité d'eau absorbée.

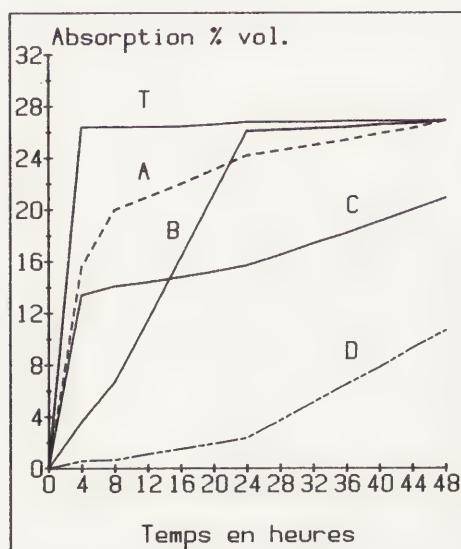


Figure 12 : Eprouvettes consolidées :
absorption d'eau
en fonction du temps.

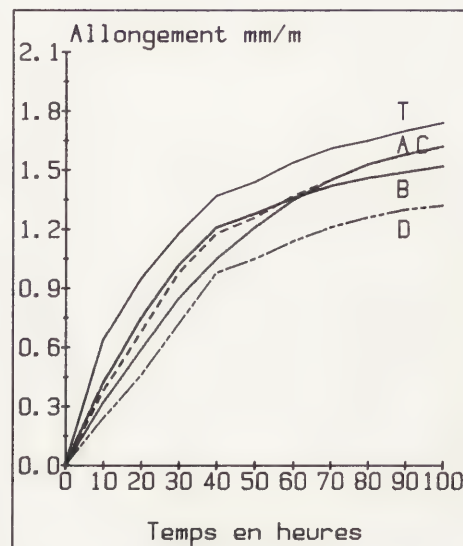


Figure 13 : Eprouvettes consolidées :
dilatation hydraulique
linéaire en fonction du
temps.

4.5. Essai de simulation à l'eau de pluie

Un essai simulant l'effet de l'eau de pluie, principal facteur de dégradation, a été conçu afin de tester les divers procédés envisagés pour la rénovation de la fresque. Il s'agissait en particulier de savoir s'il était préférable de consolider le mortier de chaux avant ou après l'application des couleurs. La préparation et le conditionnement des éprouvettes pour cet essai ont été faits de la manière suivante :

- application d'un enduit de mortier à la chaux d'une épaisseur de 1 cm sur des plots en ciment de 20x50 cm
- application à la fresque d'une couleur verte
- séchage à 20°C et à une H.R. de 40% durant une semaine
- carbonatation artificielle avec du CO₂

Le traitement de ces éprouvettes a été réalisé selon le procédé décrit ci-dessous. Dans la série C/P, la consolidation du mortier avec les silicates d'éthyle précède l'application et la fixation des couleurs, tandis que dans la série P/C, elle lui succède (C = consolidant; P = peinture).

Série C/P

- consolidation avec les silicates d'éthyle (1.9 - 2.6 kg/m²)
- séchage durant 30 jours
- application d'une peinture silicatée, jaune ou verte, sur chaque moitié de l'éprouvette
- séchage durant 3 jours
- fixage des couleurs avec un produit à base de silicate

Série P/C

- application d'une peinture silicatée, jaune ou verte, sur chaque moitié de l'éprouvette
- séchage durant 1 jour
- fixage avec un produit à base de silicate
- séchage durant 3 jours
- consolidation avec les silicates d'éthyle (1.2 - 1.5 kg/m²)

Un mois après traitement, les éprouvettes ont été soumises, alternativement, à une pluie artificielle de 1 litre/m² par heure et à un séchage à l'air à une température de 20°C, à une humidité relative de 80% et à une vitesse de l'air de 1-2 m/s à un mètre de la surface.

Afin de conserver comme référence une zone protégée du ruissellement de l'eau, ces éprouvettes ont été recouvertes, sur leur partie supérieure, par une feuille d'aluminium.



Figure 14
Vue partielle de l'installation de simulation de pluie et des éprouvettes soumises au test.

La pluie a été réalisée au moyen d'un appareil automatique, constitué d'un banc d'essai et d'un générateur mobile d'eau qui projette régulièrement des gouttelettes sur les éprouvettes et sur un pluviomètre (fig. 14). L'essai a été arrêté après une pluie cumulée d'environ 230 l/m², ce qui correspond, après estimation, à environ 10 ans de pluie sur la fresque. Cette quantité représente 2% de la pluie tombant au sol à Neuchâtel, soit 1080 l/m² par année.

4.6. Résultats

4.6.1. Aspect des éprouvettes avant l'essai

Série C/P

Dans cette série on constate, après un mois, un assombrissement général des couleurs, particulièrement marqué dans le cas du *Keimsilex*; cet assombrissement, surtout visible sur la bande témoin, est en relation avec le durcissement inachevé des consolidants. Cependant, la tonalité générale semble s'éclaircir avec le temps.

Série P/C

L'assombrissement des couleurs est nettement moins prononcé que dans la série précédente. Le consolidant, appliqué en dernier, provoque un certain blanchissement de la surface bien visible sur les éprouvettes traitées avec le *Monumentique* et le *Wacker OH*.

4.6.2. Aspect des éprouvettes après l'essai

Série C/P

À l'exception des éprouvettes consolidées avec le *Keimsilex*, l'eau provoque un éclaircissement de la couleur mis en évidence par les bandes de protection. Les éprouvettes traitées avec le *Monumentique* et le *Wacker OH* présentent un écaillage de la couche picturale, tandis que celles consolidées avec le *Motema 28* montrent de petites craquelures sans écaillage.

Série P/C

L'eau éclaircit la couleur et fait quasiment disparaître le blanchissement initial. La couche picturale de toutes les éprouvettes n'est pas endommagée et on ne remarque pas les craquelures et les écailllements observés dans la série précédente.

De toute évidence, il ressort de l'essai que l'ester de silice appliqué en dernier, système P/C, confère à la couche picturale une meilleure tenue à l'eau. Le tableau III résume les comportements esthétique et technique des produits testés.

appréciation		Keimsilex	Monumentique	Wacker OH	Motema 28
technique	vitesse de séchage	+++	++++	+++	+
	effet consolidant	++++	++	+++	+
	absorption d'eau après 42 jours	++	++	+++	++++
	dilatation hydraulique après 100 heures	++	++	++	+++
esthétique	changement de couleur avant l'essai de pluie *	++	++	++	+
	changement de couleur après l'essai de pluie *	++	+	++	+
	blanchissement avant l'essai de pluie *	++	+++	+	++++

Tableau III : *Appréciation technique et esthétique des divers consolidants; le nombre de croix est fonction du plus ou moins bon comportement (* = série P/C).*

5. CONCLUSIONS

Les résultats des essais effectués montrent que la consolidation d'un mortier à la chaux ayant une faible cohésion est parfaitement réalisable au moyen d'esters siliciques.

Les propriétés intrinsèques du consolidant ont toutefois une incidence certaine sur les caractéristiques du mortier renforcé. Le temps de durcissement du produit, le comportement mécanique et les propriétés vis-à-vis de l'eau du mortier traité sont des éléments à considérer pour opérer un choix judicieux.

D'autre part, dans le cas particulier de la rénovation de l'oeuvre de H. Erni, l'application du produit, avant ou après celle des couleurs et du fixatif, joue également un rôle très important aussi bien du point de vue esthétique que de celui de la durabilité de la couche picturale.

L'essai de simulation de pluie, bien que ne reproduisant pas exactement les conditions réelles, montre que l'application du consolidant en dernier, c'est-à-dire après la couleur, est sans aucun doute le meilleur procédé. Il faut malgré tout souligner que les essais ont été effectués sur des composites, mortier et consolidant, dans lesquels le durcissement des produits n'était pas complètement terminé. Ceci introduit forcément quelques incertitudes.

Le traitement avec des esters de silice peut comporter aussi d'autres inconvénients tels que le changement de tonalité et le blanchissement dû à un excès de produit à la surface. D'autre part, une trop faible quantité de produit risque de ne pas amener au renforcement souhaité de l'enduit. Dans le cas considéré, la consommation devrait se situer entre 1 et 2 kg/m² par cm.

Ces inconvénients peuvent être éliminés, ou du moins fortement réduits, en utilisant une quantité importante de produit dilué. Il faut surtout éviter l'application de produit par petites quantités et à l'état concentré. Une concentration excessive de matière à la surface doit être immédiatement enlevée, avant séchage, en l'épongeant avec du solvant, si possible le même que celui contenu dans le produit employé.

Sans ces précautions, mis à part l'assombrissement de la couleur, il y a risque de formation d'un voile de silice blanchâtre dont l'élimination peut s'avérer très difficile.

En conclusion, les résultats des essais montrent que la consolidation de l'enduit dégradé est possible et indiquent le procédé le plus approprié pour la réfection de la couleur. Toutefois, dans ce cas, la pluie constituant un facteur de dégradation très important avec des dommages prévisibles à long terme, il est indispensable de protéger des intempéries l'oeuvre rénovée dans son ensemble.

6. BIBLIOGRAPHIE

- /1/ Gabus, J.
Les fresques de Hans Erni ou la part du peintre en ethnographie
Neuchâtel : La Baconnière, 1955, 22
- /2/ Gabus, J.
Hans Erni et l'ethnographie
Zeitgenossen sehen H. Erni, Freudenstadt, Wien : Kunstkreis,
Luzern, 1972, 154-156
- /3/ Stähli, M.
Conservation et rénovation de la fresque Erni
Ville de Neuchâtel - Bibliothèques et musées, 1982, 135-149.
- /4/ Furlan, V. et Pancella, R.
*Propriétés d'un grès tendre traité avec des silicates d'éthyle
et un polymère acrylique*
The Conservation of Stone, II, part B,
published by Centro Conservazione Sculture all'Aperto, Bologna,
1981, 645-663.
- /5/ Pancella, R. et Furlan, V.
Propriétés d'un grès tendre traité avec des résines synthétiques
Chantiers, 16, 4/85, 295-298, première partie,
Chantiers, 16, 5/85, 409-413, deuxième partie.
- /6/ RILEM
*Essais recommandés pour mesurer l'altération des pierres et
évaluer l'efficacité des méthodes de traitement*
Matériaux et Constructions, 13, 1980, 175-252.
- /7/ Furlan, V. et Pancella, R.
*Effects of water on the properties of a calcareous sandstone
consolidated with synthetic resins*
Materials Science and Restoration, International conference,
Septembre 1983, Esslingen/Germany, Editor F.H. Wittmann,
Edition Lack + Chemie, 335-340.

RESUME

Pour empêcher que les coulis utilisés en injection de refixage des enduits ne s'échappent par des fissures, l'auteur propose une méthode de colmatage à l'aide de papier japonais et d'une colle pour photos.

L'USAGE DE "COLLE-PHOTO" DANS LA RESTAURATION DES PEINTURES MURALES

Walter SCHUDEL
Historien d'art, restaurateur
Bijlokevest, 141
B9000 GAND
BELGIQUE
Tél. : (091)25.61.62.

Dans notre pays, surtout au moment de la réforme, mais aussi après, la plupart des peintures murales ont été badigeonnées. En conséquence, si on restaure un bâtiment historique, on fera des sondages dans le but de les retrouver. Mais le temps qui s'écoule entre les sondages, le dégagement et la restauration peut être considérable. Nous utilisons des nattes de fibre de verre pour protéger les sondages pendant ce temps (1). Les nattes ont des mesures légèrement plus grandes que les sondages et sont collées à l'aide de papier collant ou de "colle-photo" sur les bords des sondages (2).

La "colle-photo" de la marque "Velpon" se compose de 15 % cis 1,4 polyisoprène dans le n-hexane (6). La résine n'est pas stable. Ceci veut dire qu'elle jaunit et qu'elle a tendance à former des pontages (cross-linking). Bien que la colle ne soit pas acide, elle ne peut donc être utilisée dans le domaine de la restauration que pour des applications temporaires. Nous croyons que l'usage décrit ici pourrait constituer une application intéressante.

Mais cette colle peut avoir aussi une autre application.

Si on doit fixer des enduits qui se détachent du mur il y a deux grands problèmes :

1. - faire pénétrer l'adhésif (sans ou avec charge) à l'endroit désiré (ce problème n'est pas discuté ici)
2. - empêcher l'adhésif d'échapper par des fuites.

Il y a plusieurs méthodes pour résoudre ce dernier inconvénient. Il est possible de boucher les fissures et trous à l'aide d'ouate. On risque, cependant, d'abimer les bords. C'est surtout le cas quand les ouvertures sont étroites ou l'enduit très mince. Aussi la plasticine peut rendre service. Mais si l'adhésif en solution aqueuse échappe quelque part malgré tout, on est perdu, parce que l'on n'arrive pas à colmater le trou avec ces matériaux hydrophobes.

Une autre possibilité est de coller du papier japonais avec de la carboxy méthylcellulose, le Paraloid B 72, etc.. sur les fuites. Inconvénients : le premier adhésif est soluble dans l'eau, le second n'est pas toujours facile à enlever.



Fig. 1



Fig. 2

La "colle-photo" nous offre quelques possibilités. Cette colle est destinée à coller des photos sur papier (album) en laissant la possibilité de les enlever facilement et sans dégâts. Les restes de la colle sur la photo ou sur le papier peuvent être enlevés par un léger frottement avec le doigt (3). La colle pénètre donc très peu ou pas et, ce qui est important, n'est pas soluble dans l'eau. On procède de la façon suivante : des morceaux de papier japonais, un peu plus larges que les fissures (trous) qu'ils doivent couvrir, sont appliqués à l'aide d'un pinceau et de l'eau (fig. 1). Ainsi il s'adaptent à la surface de la peinture. Une fois que l'eau est presque évaporée la "colle-photo" est brossée sur le papier japonais (4), spécialement où il couvre les bordures des fissures (5). Après l'évaporation du solvant de la "colle-photo" on commence à injecter l'adhésif. Les morceaux de papier japonais sont enlevés dès que l'adhésif ne coule plus, par simple déroulement (fig. 2), ou si la couche picturale manque de cohésion, après humectation avec du white spirit.

Bien qu'en général les résultats soient encourageants, surtout si l'enduit est mince et la couche picturale sensible à l'eau, il est certain qu'il y a des cas où une autre méthode est indiquée. Par exemple quand il y a un risque que des traces de colle restent sur la peinture.

NOTES

1. Les nattes de fibre de verre protègent les sondages contre la poussière, l'eau (dans certaines limites), tandis qu'elles laissent passer la vapeur d'eau. On voit, sans difficulté, la peinture à travers les nattes, formant ainsi une barrière psychologique, pour ceux qui seraient tentés de dégager un peu de la peinture.

2. C'est notre collègue E. TJEJBES qui nous a proposé d'utiliser la "colle-photo" pour ce but.

3. La colle a un Tg () assez bas, ce qui fait qu'elle reste plus ou moins molle aux températures ambiantes

4. On empêche ainsi que la colle soit brossée dans les cavités de la surface.

5. Le poids du papier et de la quantité de colle utilisés dépendent de la morphologie des ouvertures, de la quantité d'adhésif injecté, etc..

6. Les analyses sont faites par Dr. E. De WITTE (I.R.P.A.). Nous lui devons également des informations sur les propriétés de cette colle synthétique.

() Tg = Température de gel

Working Group 16

Resins: Characterization and Evaluation

Résines: Caractérisation et évaluation



MEMBERS

A. Baer (USA)
J. Blyth (USA)
H. Burgess (Canada)
Ch. Costain (Canada)
R. de la Rie (USA)
A. Diethelm (Switzerland)
J. Down (Canada)
D. Dwyer (USA)
R.L. Feller (USA)
F. Flieder (France)
R. Lafontaine (Canada)
S. Lee (Great Britain)
L. Masschelein-Kleiner (Belg.)
W. Mourey (France)
I.V. Nazarova (USSR)
T. Nishiura (Japan)
J. Petit (France)
F. Piacenti (Italy)
F. Preusser (USA)
W. Roelofs (The Netherlands)
M. Sawada (Japan)
L. Van Zelst (USA)
Ph. Weil (USA)
R. White (Great-Britain)
S. Williams (Canada)

TRIENNIAL OVERVIEW

Coordinator
E. De Witte
(Belgium)

Assistant Coordinator
N. Tennent
(Scotland)

PROGRAMME 1985-1987

1. Interlaboratory programme to test light aging apparatus, consisting of a questionnaire on laboratory apparatus and techniques; distribution, aging and analysis of samples; and publication of information obtained.
2. Continuation of the chemical identification of synthetic resins used in conservation.
3. Analysis of natural resins used in conservation and investigation into means of stabilizing them.

SUMMARY

It is hopeful to see that the interest in varnishes still concerns deeply conservators and scientists. As well the documentation of naturally aged varnishes as the results of laboratory research will be a matter of discussion.

Investigations on the use of synthetics in new fields, such as the consolidation and fixing of very matt paint layers are started. The stability of resins used in stone conservation is a constant source of concern.

Most of the answers on the questionnaire about light aging apparatus are gathered. The distribution of the samples will start shortly.



SUMMARY

The aim of this work is to study the stability and durability of some methylphenylsiloxane polymers used for the treatment of stone. Therefore polymers spread on various kind of supports were exposed to U.V. light in order to achieve an artificial ageing and to control if the decay was similar to that of some samples coming from the S. Marco Basilica (Venice). The samples were then analyzed by I.R. spectroscopy, by contact angle measurements and by SEM technic. In this paper the variations of chemical structure and of water-repellence after ageing of the polymers are discussed.

STABILITY STUDY OF SILICONIC RESINS EMPLOYED IN THE STONE CONSERVATION

G.Biscontin^o, C.Botteghi[^], C.Dalla Vecchia[^], G.Driussi, G.Moretti, A.Valle^o

^o:Università di Padova (Italy)

[^]:Università di Venezia (Italy).

Dorsoduro 2137 - 30123 VENEZIA (Italy).

Introduction

The aim of this work is to check the stability of some usual protectives used for the conservation of the exposed stone materials. Among the most used siliconic polymers we have studied two polymers (polymethylphenylsiloxanic resins):

- i) resin A: 11309 (Rhône-Paulenc)
- ii) resin B: XR 893 (Rhône-Paulenc).

These two products are widely employed because their peculiar properties (1):

- 1) The Si-O-Si bond gives a sufficient compatibility and a good adherence to stone material;
- 2) the Si-O bond energy is higher than that of C-C bond of similar non-siliconic products: therefore, these resins are generally more stable than, for example, the acrylic ones;
- 3) alkylic and/or phenylic groups provide these resins with a high hydrophobicity degree and with a remarkable water-repellence.

Moreover, the presence of phenylic groups ensures to the polymer elasticity, flexibility and stability (2,3).

Experimental

The resin separation from the support for the preparation of I.R. samples results to be particularly difficult. This has been overcome carrying out the irradiation experiments on a resin film applied on a KBr pellet and submitting it directly to I.R. analysis. In this way resin modification at various times of U.V. irradiation could be followed.

The work is carried out in two phases:

- i) The resin are supported on neutral holders such as glass and KBr pellet and on stone of different nature slabs: Istria stone, Carrara marble, Vicenza stone. All the samples have been aged by exposition at increasing times in an U.V. camera Mod. INVE equipped with a 500W Hg lamp at 25 cm., following a methodology frequently used in polymer decay studies. After each ageing cycle the samples have been examined both by chemical-physical tests in order to control the degree of polymeric decay and to estimate the corresponding variation of the physical properties.
- ii) Some samples coming from the marble sculpture of the Central Façade of the S. Marco Basilica have been examined. These samples have been treated with resin B during a repair work in 1976. The analyses results on these samples have been compared with those obtained in laboratory tests to verify if the artificial ageing occurs by the same mechanism as that of the natural process. The samples are some marble fragments, some superficially polymerized resin drops and statue fragment treated at the same time and in analogous way but kept indoors.

For this study, the investigation and the control tests are:

- a) I.R. spectroscopy;
- b) Scanning Electron Microscope (SEM) observations;
- c) Contact-angle measurements.

Results and Discussion

a) I.R. Analyses

The I.R. data obtained for resin A on KBr are shown in Fig.1. Spectrum A is referred to pure resin A and spectrum B is relative to the 48 h aged resin. The comparison between the absorption bands before and after ageing point out the following outcomes:

- i) the absorption band of the -O-H bond (ca. 3400 cm^{-1}) intensifies with increasing exposition times;
- ii) phenylic bands (1600 and 1430 cm^{-1}) gradually decrease up to nearly total disappearance after 48 h (spectrum B);
- iii) also the bands connected with the Si-C₆H₅ bond (1135 , 1000 and 490 cm^{-1}) gradually decrease with increasing exposition time;
- iiii) in the carbonyl group absorption range (1800 - 1600 cm^{-1}) a set of weak bands appears: its intensity increases with the ageing time of the sample.

These first results indicated that phenylic groups bonded to silicon atom are implicated in the progressive decay caused by the U.V. radiations. A further experimental evidence is provided by the fact that polydimethylsiloxanic resin do not show similar phenomena, that there are no appreciable structural modifications after U.V.

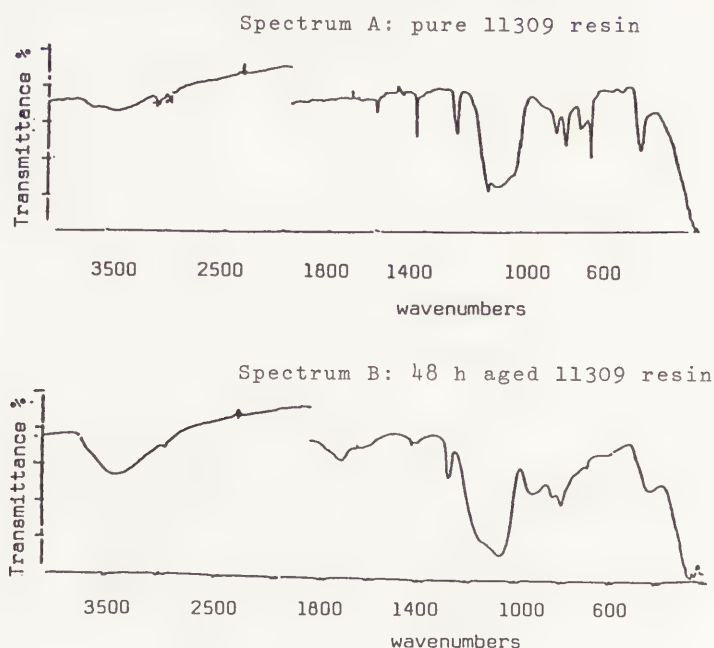


Fig. 1

radiation under analogous conditions (4).

Moreover, the remarkable changes observed in the resin A in the 1000-600 cm^{-1} zone for aged samples are to attribute to polymer cross-linking.

The tests on resin B show spectral variations in the polysiloxanic field analogous to those observed for the resin A.

Some other tests have been done on glass slabs to obtain more reliable data and to relate these to the resin thickness. The products A and B have been applied by a drawing-film apparatus to prepare samples with homogeneous and constant thickness.

After a U.V. exposition of 48 h, all the resin shows a yellow coloring and they do not completely solubilize when treated by most solvents.

Comparison between I.R. analysis of the soluble part and of the insoluble one shows that insolubility is directly connected with the polymer cross-linking.

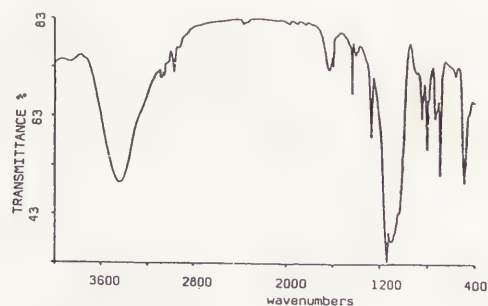


Fig. 2: Soluble part

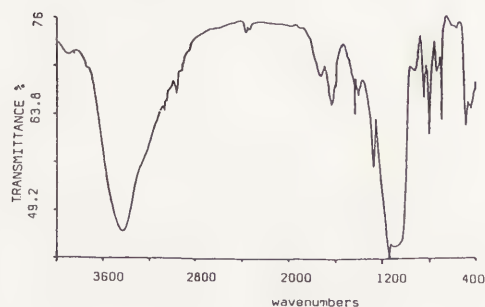


Fig. 3: Insoluble part

Examining Fig. 2 and Fig. 3 one can point out that the soluble fraction (Fig. 2) does not show remarkable changes in comparison with pure resin, while the insoluble part (Fig. 3) appears to be cross-linked, even if to a small extent. The findings in the above described experiment is furtherly confirmed: an increase of the $-O-H$ stretching bands and a decrease of the $Si-C_6H_5$ bands are also noticed.

The solvents used are not able to extract all the resin from the natural stone samples, analogously to what happened with the samples on glass slides. In fact, the most decayed part remains almost entirely on the stone slab.

A small alteration, which is slightly different for the various stone materials used has been observed. The I.R. analysis on resin A carried out on the extract from Vicenza stone specimens show very low variations in comparison with the unaltered resin, while the extracted fraction from Istria stone looks pale yellow after ageing showing small, but significant decay features.

A further test has been carried out on Carrara marble samples treated with resin B. The yellow polymer retained by the stone support after solvent extraction has been mechanically removed and submitted to I.R. analysis. The spectrum reported in Fig. 3 after subtraction of the strong bands of $CaCO_3$ shows some decrease of the bands connected with the benzenic ring, as well as a definite variation of the $Si-O-Si$ and of the $Si-C_6H_5$ groups absorption. The I.R. spectra of the three samples from the 6^5S Marco Basilica, carried out with the above method, are reported in the Fig. 4-6. From examination of these spectra, looking at the intensity ratios of aromatic and aliphatic $-C-H$ stretching bands, it can be drawn that the decay connected to the phenylic group is more marked for the outdoor stored samples (Fig. 4). This is furtherly supported by the decrease of the bands at 1593 cm^{-1} and by the fact that such spectrum becomes similar to that one of a polydimethylsiloxanic resin.

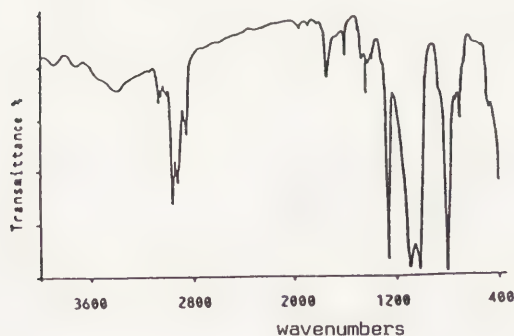


Fig. 4: outdoor
stored sample
(resin XR 893)

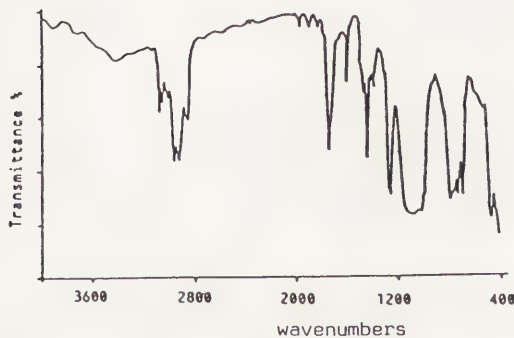


Fig. 5: indoor
stored sample
(resin XR 893)

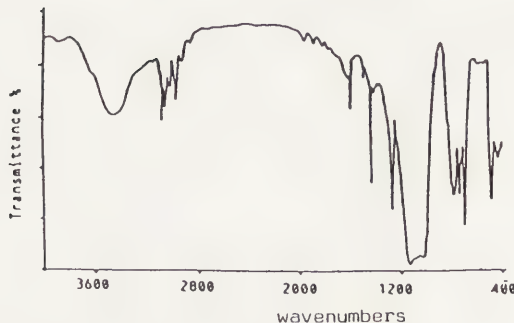


Fig. 6: drops
(resin XR 893)

Moreover it is interesting to note that the resin drops do not suffer appreciable decay, even if they present a pale yellow colouring too. As expected, decay phenomena concern the most superficial layer only for high polymer thickness. In other words, a small fraction only, in comparison with the whole polymer, decays. Thus, both pure resin A and resin B suffer evident decay phenomena when submitted to U.V. radiations. Both U.V. and naturally aged resin samples present a highly cross-linked fraction and a yellow colour. This implies a partial irreversibility of the resin itself. The phenyl radical, when detached from chain, can react with the atmospheric oxygen producing phenols. These can be further oxidized to yellow quinone-like compounds, as found for another kind of polymer containing aromatic group (5). In fact, the carbonylic bands, detected in the range from 1630 to 1680 cm^{-1} could be attributed to the quinone-like chromophores presence. As far as the products performance and durability are concerned the study has pointed out that artificially aged samples show a wide system of microfractures. Moreover this phenomenon further proceeds, till at partial detachment of the surface film, takes place on samples coming from the S. Marco Basilica. On the contrary, the water-repellence decreases with ageing time. This fact, even if undesired, does not invalidate the protective properties of these polymers, at least for artificially aged samples. Anyhow further experiments are in progress. Even if we are not able at this point of the work to propose a reasonable decay mechanism based on these experimental data, one can assert that phenylic groups of resin A and B are progressively detached from the polymer chain by the U.V. radiation at an appreciable degree. In other words the aromatic system introduced in the polymer framework to improve the technical performance of these products constitute also a preferential site for the attack of the U.V. light. The free radicals formed by this process then cause extensive polymer photodecomposition.

b) SEM observation

Some samples have been subjected to SEM observation in order to investigate on protective film morphology and on its alterations. This technique allows to value the morphological characteristics both of the product (that is: uniformity, thickness, etc.) and of the stone material-protective system as whole (coating degree, adhesion and distribution of polymer, etc.) (5,6). The collation of Fig. 7,

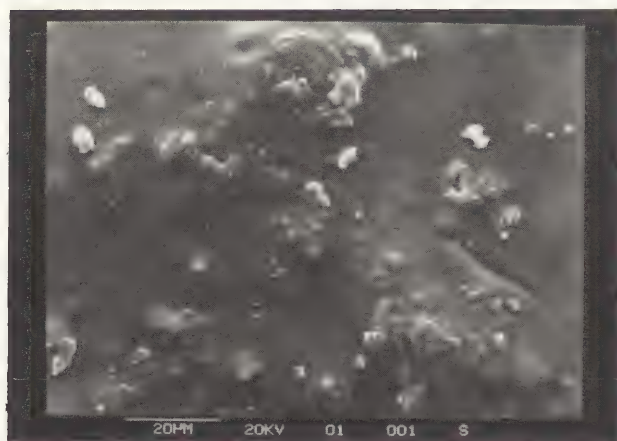


Fig. 7: Istria Stone: pure resin A



Fig. 8: Istria stone: resin A 24 h aged

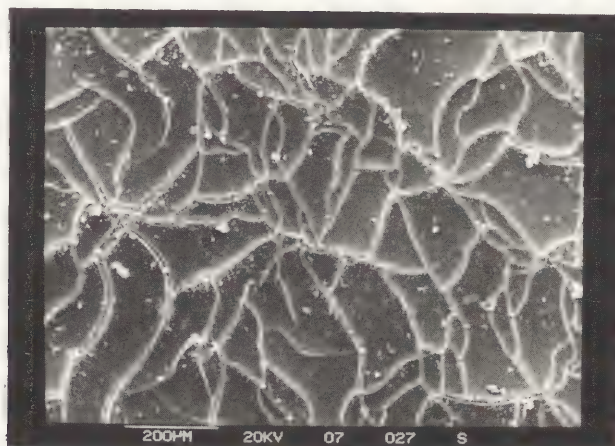


Fig. 9: Istria stone: resin A 48 h aged

Fig. 8 and Fig. 9 (photos respectively executed on pure resin A, after 24 h and after 48 h of ageing) can clarify that Istria stone treated with this resin has initially a good coating, even though with the unavoidable heterogeneity due to the wrinkledness of material. Fig. 8 represent the same test after ageing of 24 h: it is possible to note some break lines. These lines, however, do not interest the whole thickness of the polymeric film which is compact enough. The phenomenon is even more evident in Fig. 9: after a 48 h ageing, fractures concern most of the surface and the resin film begins to break. The behaviour of the Carrara marble samples is analogous. Vicenza stone, just because of its conformation, does not permit the formation of a superficial film. So, the same phenomenon does not occur, but resin efflorescences appear after 48 h. This strongly suggest an initial cohesion loss. SEM investigations carried out on sample from S. Marco statues point out both a generalized cohesion loss of polymeric film and gypsum crystals formation just in the resin fractures (Fig. 10).

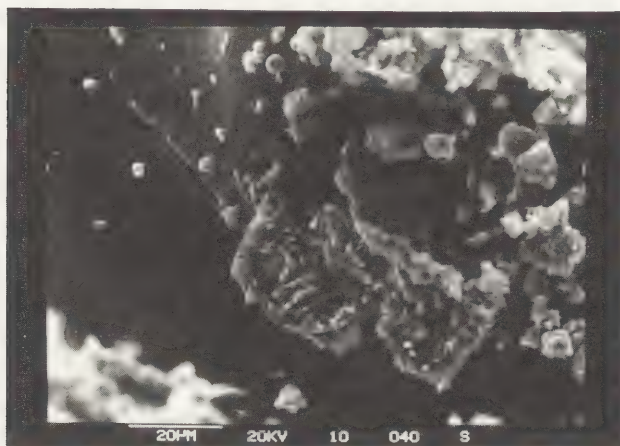


Fig. 10: S. Marco Basilica sample (resin B)

c) Contact-angle measurements

The aim of this study is also to connect chemical aspects of polymer decay with their eventual efficacy loss. The water-repellence has been chosen as a parameter in order to verify this fact. For this purpose the contact-angle of aged samples have been measured following a well known method (1).

Tab. 1: Contact-angle (θ) measurements

ageing time ↓	VICENZA STONE	ISTRIA STONE	CARRARA MARBLE
0	124°	83°	82°
24 h	111°	82°	74°
48 h	105°	76°	71°

The analysis of the results (Tab. 1) point out that contact-angle, directly connected to the product water-repellence, tendentially decreases with ageing. Moreover it necessarily depends on resin surface layer, which in turn is connected to stone porosity. For Vicenza stone this occurs in a more appreciable way in the initial phase of ageing (24 h) and the water-repellence tends to achieve a "plateau" with rather high values after 48 h yet. The behaviour of the Carrara marble samples has a quite similar trend, but with both initial and final values decidedly lower. On the contrary Istria stone samples show a quite different behaviour: the contact angle remains almost unchanged up to an 24 h U.V. exposure, and then it markedly decreases for still greater ageing times. Moreover one can foresee a further water-repellence loss for still longer time.

BIBLIOGRAPHY

- 1) A.A. V.V. Synthetic Materials used in the Conservation of Cultural Property. Ed. ICCROM, Rome (1967).
- 2) R.N. MEALS and F.M. LEWIS. "Silicones". New York: Reinhold Ed. (1959)

- 3) G.G.AMOROSO. "Esters siliciques et resines silicones. Applications aux bâtiments et à la conservation de la pierre". Schweizer Baublatt, n°65 (1979). Kunststoffe im Bau n°88, p.1-7.
- 4) Our unpublished results.
- 5) G.G.AMOROSO, V.FASSINA: Stone Decay and Conservation. Amsterdam Elseviers (1983), p.12.
- 6) G.TORRACA. "Porous building materials". Rome (1981): Ed. ICCROM p.3.

SUMMARY

An overview of the results of the research on picture varnishes at The Metropolitan Museum of Art is presented. In order for synthetic varnishes to have optical properties equivalent to those of natural resin varnishes they should have low molecular weight and a relatively high refractive index. The molecular composition is of minor importance as long as varnishes of low polarity are used. In order for varnishes to be less susceptible to autoxidation reactions, certain chemical groups such as ketone groups and carbon-carbon double bonds should be absent from their molecular structures. Although the low-molecular-weight varnishes presently available are very brittle, more flexible resins with low molecular weight are feasible. The process by which dammar varnishes as well as varnishes in general degrade, is predominantly photochemical autoxidation. Yellowing of dammar is a secondary non-oxidative thermal process. Accelerated aging studies should therefore be carried out under light. Polymer stabilizers have the potential to prolong the useful lives of varnishes. Dammar may, however, be very difficult to stabilize. Care should be taken with the use of stabilizing additives since they may have negative side effects. They should not be used without thorough testing. Several new resins are under investigation at the Metropolitan Museum of Art: a derivative of ketone resin was synthesized with improved stability and flexibility; several commercially available resins with high refractive indices, low molecular weights and solubility in solvents of low polarity are being tested. Solvents for varnishes with low evaporation rates and varying concentrations of aromatics are described.

RESEARCH ON PICTURE VARNISHES: STATUS OF THE PROJECT AT THE METROPOLITAN MUSEUM OF ART

E. René de la Rie
Research Chemist
The Metropolitan Museum of Art
Fifth Avenue at 82nd Street
New York, New York 10028
U.S.A.

1 - Introduction

The varnish problem is perhaps the single most important one in painting restoration, since it is the rapid degradation of varnish layers that induces most restorations. Despite the availability of synthetic coatings, such as those based on poly(vinyl acetate) and polymethacrylates, which possess good chemical stability [1], traditional natural resin varnishes and ketone resin varnishes are still widely used. The latter varnishes autoxidize rapidly, leading to defects such as yellowing, cracking, hazing, loss of gloss, and change of solubility. The varnishes, therefore, need to be removed frequently, which, due to oxidation of the coatings, can generally be accomplished only with relatively polar (strong) solvents. These solvents, as is well known, may not only affect the varnish layer, but also the paint layers, causing swelling and leaching of the medium [1].

Varnishes alter the appearance of paintings dramatically [2]. The reason for the continued use of unstable varnish materials lies in differences in optical properties between those materials and modern clear coatings. No stable varnish with optical properties equivalent to those of traditional varnishes is available.

A research program in the Paintings Conservation Department of The Metropolitan Museum of Art focuses on all facets of the varnish problem. Thus optical properties as well as degradation processes are studied; the potential of stabilizing additives is investigated, and new resins are being synthesized; furthermore, commercially available synthetic resins with different chemical and physical properties from the ones that have been used so far are being tested.

This paper gives a summary of the results thus far obtained in the project. The results are described in detail elsewhere [2-6].

2 - Optical Requirements for Picture Varnishes

Varnishes alter the appearance of paintings by creating a (microscopically) smoother surface [2]. This reduces surface scattering of light, thus allowing for a greater portion of the light to penetrate the paint layers. Light scattered from the surface is generally white light which mixes with colored light being returned from within the paint layers. This mixing in of white light causes a desaturation of the color. Thus varnishes have the effect of producing more saturated colors (as well as more gloss). Furthermore, in a varnished picture the difference between the refractive indices of pigment and surrounding medium is reduced, since all pigments become embedded in material with a refractive index higher than that of air. This results in a reduction of the amount of reflected light, causing the colors to be darker than when the picture is left unvarnished.

Color saturation is of great importance in the appreciation of Old Master paintings. Not only were the paintings originally intended to be seen with highly saturating ("glossy") varnishes [7,8], but dark passages which have "sunk" over time can often be read only with such varnishes. Although the different appearance of paintings varnished with synthetic coatings has been mentioned in the literature several times [1,9-12], few references to the aspect of color saturation were made [1,p.47/48;12].

Synthetic polymers used for picture varnishes differ from natural resins mainly in two aspects: molecular weight and refractive index (RI). Natural resins have very low molecular weights relative to those of polymeric materials. The refractive indices of natural resins are somewhat higher than those of the polymers (see Table 1).

The difference in molecular weight leads to a large difference in solution viscosity. Solutions of natural resins have viscosities low enough for brush application at concentrations as high as 40-50% by weight. Synthetic polymers can only be applied at concentrations of 10-20% by weight. For reasons explained elsewhere [2], varnishes which have low viscosities at high concentrations form smoother surfaces over rough substrates. Low-molecular-weight (LMW) resins, therefore, often produce more color saturation than high-molecular-weight (HMW) resins.

In order to minimize reflection of light at the medium-varnish interface, varnishes should have a refractive index approximating that of the medium. No

Table 1 Molecular Weights* and Refractive Indices of Some Traditional and Modern Varnish Materials [2].

	\bar{M}_n	RI
dammar resin	488	1.539
gum mastic	460	1.536
ketone resin	442	1.529
Acryloid B72**	11,397	1.487
Acryloid B67**	10,960	1.477
AYAA ⁺	31,691	1.467
27H ⁺⁺	38,666	1.477

* The number-average molecular weight, \bar{M}_n , is given [2].

** Rohm and Haas.

+ Union Carbide.

++ Experimental varnish [1].

exact data are available concerning the refractive indices of oxidized paint media. They are likely to be relatively high compared to fresh media due to higher RIs of oxidation products. Although the small differences between the RIs of most modern materials and those of traditional varnishes have been seen in the past as too minimal to be of importance [1,10,11], there is reason to believe that they cause perceptible optical differences over paints of low reflectance [2]. De Witte et al. have demonstrated that varnishes with low viscosities as well as with high RIs receive higher scores for appearance by restorers [7].

Another potential source of light scattering are air pockets at the varnish-paint interface. These would occur if the varnish fails to make intimate contact with the paint surface. Although Feller considered lack of penetration into porous paint surfaces a cause of lighter colors obtained with HMW coatings [1,p.142;11], Thomson remarked in an early paper that he had never seen any evidence of lack of contact with modern synthetic coatings [10]. Whether varnishes make good contact with paint surfaces is determined by the difference in surface tension between the varnish and the paint surface. The surface tension of a material is related to its chemical composition. In this author's opinion, it is likely that complete contact with paint surfaces is obtained with all varnishes of practical interest, i.e. varnishes of relatively low polarity (those which are soluble in solvents of low polarity). Such varnishes are likely to have lower surface tensions than the paint surface, which is a condition that assures good contact [2]. Some modern coatings, particularly poly(vinyl acetates) have been shown to have poor adhesive strength. This may eventually cause loss of contact with the underlying paint layer. This defect, however, which occurs over time, does not explain the initial optical differences.

Thus the requirements for a varnish with good optical qualities are low molecular weight and a relatively high refractive index. To date only the natural resins, such as dammar and mastic, and ketone resins are in this category.

3 - Removal of Low and High Molecular Weight Varnishes from Paintings

An often overlooked problem associated with HMW varnishes is the difficulties which arise during cleaning. HMW resins, even if they do not cross-link, are always more difficult to remove from paintings than LMW resins. Obviously the increasing polarity with time of LMW resins currently in use is undesirable, since it makes the use of polar (strong) solvents necessary. Removal of such resins with solvents, however, is otherwise relatively straightforward. One takes advantage of the fact that these resins form solutions of low viscosity at very high resin concentrations. Thus a small quantity of applied solvent rapidly produces a solution of low viscosity. HMW resins, on the other hand, require large amounts of solvents in order to obtain solutions with manageable viscosities. With the volatile solvents generally used during cleaning, such as toluene, acetone, and alcohols, it is often difficult or impossible to create solutions of low concentrations. The result is that the varnishes come off as "sticky substances" rather than as solutions.

Another point in favor of LMW resins is that cross-linking is unlikely to have a large influence on their solubility [1,10]. As is well known, cross-linking may cause the formation of a giant insoluble network in polymeric coatings (as occurs for example in poly(butyl methacrylate) [1,10]). Although the molecular weights of natural resins and ketone resin increase during aging (see section 4), they remain very low relative to the starting molecular weights of polymers.

4 - Chemical Stability and Flexibility of Varnishes

All organic materials deteriorate due to autoxidation, which is accelerated by, among other things, ultraviolet light. If materials are applied as thin films, as are varnishes, the bulk of the material is exposed to oxygen and light (i.e. there is a high surface to volume ratio). Varnishes are, therefore, particularly susceptible to autoxidation reactions. Defects of varnishes such as yellowing, cracking, and change of solubility are all caused by autoxidation reactions.

Autoxidation is a chain reaction involving free radicals [3,4]. Once one or more free radicals are produced, the process maintains itself by creating more free radicals (i.e. the process is autocatalytic). It is well known that certain chemical groups promote autoxidation reactions. Those are, for example, carbon-carbon double bonds, ketone groups, ether oxygens, and tertiary hydrogen atoms [4]. Ketone groups are subject to scission reactions under the influence of ultraviolet light, during which free radicals are produced. Consequently, ketone groups are major photo-initiators. Natural resins and ketone resin contain an abundance of ketone groups and are therefore very sensitive to photochemical degradation. In addition, natural resins contain carbon-carbon double bonds, which easily participate in autoxidation reactions (see Figure 1). A basic requirement for a durable varnish, therefore, is the absence of such reactive groups. In addition, varnishes can be stabilized with additives which inhibit autoxidation reactions (see section 6).

The brittleness of picture varnishes has been related to viscosity grade

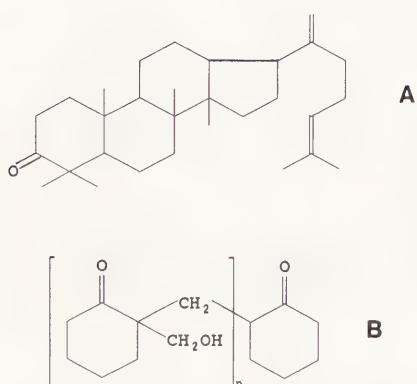


Figure 1 Typical Structures Found in (A) Dammar Resin and (B) Ketone Resin.

[1,p.127;13]. The LMW varnishes presently available are thus less flexible than coatings based on polymers. It is this author's opinion, however, that brittleness which characterizes dammar, mastic, and ketone resins, is not a necessary quality of low-molecular-weight varnishes.

There are two aspects of the brittleness of LMW resins which need to be elucidated. The lack of flexibility in these resins is the result of strong molecular interaction between their components: for the most part hydrogen bonding between carboxylic acid groups and/or hydroxy groups. In addition, the rigid cyclic structures of triterpenoids in dammar and mastic allow for relatively strong interaction between the hydrocarbon skeletons of the resin components. In fact, were it not for the hydrogen bonding in ketone resin, it would be extremely soft, or even in the liquid phase (see section 7) [6]. Secondly, the brittleness of natural resins and ketone resin increases dramatically with time. Oxidation causes the formation of products with polar groups such as carboxylic acid groups. This causes the strong intermolecular interaction to increase even further. Since this process happens very rapidly, causing a great increase in brittleness during the first years after application, it seems likely that the brittleness which conservators associate with these resins is predominantly that present after autoxidation.

A new resin for picture varnishes, therefore, should have a somewhat lower brittleness than the existing LMW resins, but it appears unnecessary to create a flexibility equivalent to that of many polymeric coatings. Thomson has even remarked in one of his papers that, if a picture varnish were too strong and flexible, the film could peel off easily once a small part has come loose; bits and pieces of a fragile paint film might also come off in the process [14].

The proper flexibility and hardness can be achieved with LMW weight resins by introducing the right amount of intermolecular interaction (see section 7) and/or by mixing in small amounts of polymeric material. Furthermore, if autoxidation can be inhibited, the increase in brittleness will be inhibited as well.

5 - The Degradation of Dammar

Despite the wide use of dammar varnishes, knowledge of their aging processes is limited. In our laboratory research has been conducted towards achieving a better understanding of these processes and the effects which stabilizing additives (see section 6) have on them [4]. The conclusions of this study are that photochemical degradation is the primary process, and that secondary nonoxidative reactions are responsible for the development of yellow chromophores. Only when light is present does extensive oxidation take place, which results, among other things, in the familiar change in solubility. The thermal reactions responsible for yellowing are secondary nonoxidative reactions between autoxidation products. Evidence has been obtained to support the thesis that they are condensation and dehydration reactions. Yellowing is easily reversed by exposure to light and therefore does not develop when aging under intense light is performed. Bleaching can be accomplished with visible light (no ultraviolet component is necessary).

It is important to distinguish between the change in solubility of LMW resins due to increasing polarity with time, and the change in solubility of polymeric coatings due to cross-linking. With aging, dammar cross-links to form a product with higher average molecular weight, however, the process does not affect the solubility of the varnish. Oxidized dammar remains soluble, although in a relatively polar (strong) solvent or solvent mixture. The change in solubility is due solely to the occurrence of polar oxidation products, particularly products containing carboxylic acid groups (see Table 2).

The findings have implications for accelerated aging studies. Although dammar does not yellow much when aged under intense light, e.g. in a xenon arc fadeometer, this is the only valid method of accelerated aging. Heat aging produces yellow products; however, yellowing is much more pronounced if heat aging (under air or nitrogen) is carried out after aging under light (see Figure 2). Autoxidation of any varnish is likely to be primarily a photochemical process [4,14]: in order to obtain thermal energy equivalent to the energy provided by ultraviolet light, temperatures over 200 °C would be required [4].

6 - Polymer Stabilizers

As others have pointed out [15-17], many stabilizing additives are available which inhibit autoxidation reactions in coatings and plastics [3]. These additives have the potential of prolonging the useful lives of varnishes as well as of other conservation materials. Many experiments have been carried out at the Metropolitan Museum with stabilizing additives; a review paper on the subject of polymer stabilizers has been prepared [3]. Of all the available additives, hindered amine light stabilizers (HALS) and benzophenone and benzotriazole type ultraviolet absorbers are the most promising for varnishes [3]. Incorporation of stabilizers in newly formulated varnishes will be virtually a requirement. Experiments with dammar resin, however, demonstrate that stabilization is difficult to obtain with this resin. Irganox 565 [15,16] is not recommended as an additive for dammar varnishes, since it breaks down rapidly in conditions where light is present. It may also cause additional

Table 2 Acid Values of Dammar Before and After Aging [4].

unaged	39
474 hours 100 °C	54
461 hours fadeometer	85

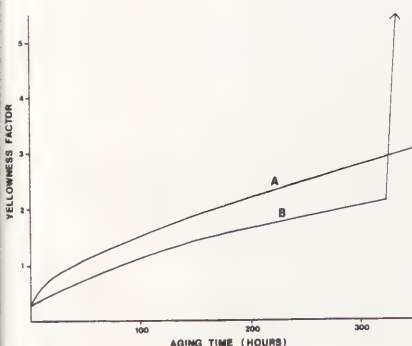


Figure 2 Yellowness Factor of Films of Dammar Resin During Accelerated Aging [4]. (A) Oven 100 °C; (B) Xenon-arc fadeometer, followed after 323 hours by oven 100 °C.

yellowing of the varnish due to yellow breakdown products of the additive [5]. Ketone resin varnishes may benefit from the incorporation of HALS and ultraviolet absorbers, although some negative side effects such as wrinkling of the surface have been noticed. Experiments with dammar and ketone resin are still in progress at the Metropolitan Museum.

A few words of caution with respect to the use of polymer stabilizers in general seem to be in order. Care should be taken in choosing additives since stabilizers may have negative effects, notably staining by either the parent product or decomposition products of the additive, and exudation of the additive at the surface. Furthermore, it should be kept in mind that polymer stabilizers have been developed for use in coatings with inherently greater stability than traditional varnish materials. Consequently, stabilizing additives should be thoroughly tested and scrutinized for negative side effects in appropriate accelerated aging experiments, before being used in conservation materials. In order to avoid volatilisation of the additives only stabilizers with high molecular weight should be used. Chemical compatibility of stabilizers and varnishes is a further requirement; otherwise, migration and/or exudation of the additives may occur [3].

7 - Synthesis of a derivative of ketone resin

Ketone resins such as AW2, Ketone Resin N, Laropal K80 and MS2 have been popular as replacements for natural resins since the 1950s. (Laropal K80 (BASF) is the only one currently available.) They have low molecular weights and high refractive indices (see Table 1) and consequently approach the optical properties of natural resins. Although these resins do not yellow as much as natural ones, they are nevertheless not very stable [6,14]. Autoxidation causes a rapid change of solubility similar to that found in dammar. Furthermore, matt spots in the surface may develop as a result of microscopic wrinkling. Another shortcoming of ketone resins is their brittleness.

At the suggestion of the National Gallery in London reduced forms of MS2 and AW2 were produced by the manufacturer of MS2. These were available under the names MS2A and MS2B. Recently MS2A has become available again. In these products the ketone groups are reduced to hydroxy groups, leading to a lower autoxidation rate. Because of an increase in the number of their hydroxy groups these reduced resins are even more brittle than the parent products.

In our laboratory a product has been synthesized which has both increased stability and increased flexibility [6]. Using Laropal K80 as the starting material all ketone groups were reduced and subsequently a portion of the hydroxy groups were esterified. Reduction of the ketone groups insures improved stability, while partial esterification provides for a reduction of brittleness. By choosing the proper degree of esterification a product was obtained with intermediate hardness. (Esterification of all hydroxy groups leads to an extremely soft product.) In accelerated aging tests the product was shown to have much improved stability over ketone resin (as well as MS2A). The product is soluble in hydrocarbon solvents with an aromatic content of about 40%. Tests for workability and appearance on paintings gave positive results. The product, both with and without stabilizing additives, is still being tested at the Metropolitan Museum for long term aging behaviour. During preliminary discussions a manufacturer of synthetic resins has expressed interest in producing the resin on a pilot plant scale for the conservation field.

8 - Commercially Available Resins.

A few commercially available resins which combine very promising properties have been found. These are resins with relatively high refractive indices, low molecular weight, solubility in solvents of low polarity, and good chemical stability. Some are soluble in purely aliphatic hydrocarbon solvents.

Experiments with these resins are in progress at the Metropolitan Museum. Some of the products have shown outstanding stability and good workability as well as good optical properties when applied to paintings.

At this stage it is too early to recommend any of these products, since aging and other tests are still under way in the Museum. It must be said, however, that these resins have very promising properties indeed and that future application as varnishes on paintings is in the realm of possibility.

9 - Solvents for Varnishes

In order to be applied with a brush, varnishes need to be dissolved in solvents with relatively low evaporation rates. Mineral spirits (white spirit) and oil of turpentine have suitable evaporation rates for such applications. (Oil of turpentine is not recommended for use with stable resins, since this solvent is rather prone to autoxidation itself: some solvent is retained by varnishes for extended periods of time.) Ideally, varnishes should be soluble in purely aliphatic solvents. As mentioned above, several commercial resins under investigation at the Metropolitan Museum fulfill this requirement. The ketone resin derivative synthesized in our laboratory, however, requires a solvent

Table 3 Evaporation Rates and Aromatic Content of Several Hydrocarbon Solvents

	aromatic content (%)	boiling range (°C)	seconds to 90% evap.
toluene	100.0	111	234
xylene	100.0	137-140	770
diethylbenzene	100.0	180-182	---
Shell min.spir. 135*	16.5	166-203	5,250
Shell min.spir. 150-EC*	3.6	163-207	4,490
Shell TS-28 solvent*	76.0	167-193	4,210
Shell Cyclo Sol 53*	99.4	163-176	3,285
Shell Cyclo Sol 63*	97.5	181-202	11,550

* Data from Shell; the evaporation rates for toluene and xylene are also data provided by Shell.

with an aromatic content of about 40%. The very stable acrylic resin Acryloid B72 (Rohm and Haas) [1], which can be used for paintings that do not require a high degree of color saturation, needs a solvent which is virtually 100% aromatic. Mineral spirits usually contain 16-17% aromatics (although mineral spirits much lower in aromatic content are available as well). The aromatic solvents toluene and xylene, besides being toxic, have evaporation rates which are much higher than those of mineral spirits, and therefore are not suitable for brush application. Diethylbenzene evaporates much more slowly than toluene or xylene, but it is generally disliked by conservators because of its unpleasant odor.

There are industrial hydrocarbon solvents which contain high concentrations of aromatic compounds. These aromatic compounds are higher derivatives of benzene, which insures the right evaporation rate and low toxicity. Some examples of hydrocarbon solvents manufactured by Shell are given in Table 3. Other manufacturers carry similar solvents. An aromatic content of about 40% is obtained, for example, with a 60/40 mixture of Shell mineral spirits 135 and Shell TS28 solvent. A 75/20 mixture would dissolve dammar resin, which requires an aromatic content of about 30%. (Shell Cyclo Sol 53 and Shell TS-28 Solvent were suggested before as solvents for dammar by Lafontaine [15]; however, it is unlikely that the replacement of oil of turpentine by these solvents gives much improvement of the stability of dammar varnishes [4].)

Mixtures of mineral spirits and TS28 used at the Metropolitan Museum have demonstrated good workability. Aging tests with films of the ketone resin derivative prepared from solutions in this solvent mixture gave results close to those with films prepared from solutions in reagent grade toluene. For resins which require an aromatic content of 100%, such as Acryloid B72, Shell Cyclo Sol 53 or 63 could be used (although the latter has a very low evaporation rate). These solvents can also be used in cleaning paintings. It should be kept in mind, however, that owing to their lower evaporation rates they linger longer in the paint film than solvents such as toluene.

Acknowledgements

The author is grateful to John M. Brealey, Chairman of the Paintings Conservation Department of The Metropolitan Museum of Art, for making this work possible and for his constant encouragement. Much of the work described in this paper would have been impossible without the help of Christopher W. McGlinchey, who carried out many of the experiments. The synthetic work described in section 7 was carried out by Alexander M. Shedrinsky. The author is grateful to the staff, fellows and interns of the Paintings Conservation Department of the Metropolitan Museum of Art for helpful discussions and comments on the manuscript.

REFERENCES

- 1 Feller, R.L., Stolow, N., and Jones, E.H., On picture Varnishes and their Solvents, revised and enlarged edition, National Gallery of Art, Washington D.C. 1985.
- 2 De la Rie, E.R., The Influence of Varnishes on the Appearance of Paintings, Studies in Conservation 32 (1987), 1-13.
- 3 De la Rie, E.R., Polymer Stabilizers. A Survey with Reference to Possible Applications in the Conservation Field, submitted for publication to Studies in Conservation.
- 4 De la Rie, E.R., Photochemical and Thermal Degradation of Films of Dammar Resin, submitted for publication.

- 5 De la Rie, E.R., An Evaluation of Irganox 565 as a Stabilizer for Dammar Picture Varnishes, submitted for publication.
- 6 De la Rie, E.R., and Shedrinsky, A.M., The Chemistry of Ketone Resins and the Synthesis of a Stable, Flexible Derivative, in preparation.
- 7 Eastlake, Ch.L., Methods and Materials of the Great Schools and Masters, Vol. I, Dover Publications, Inc., New York 1960, i82.
- 8 Ruurs, R., Matt oder glänzend?; Gemäldefirnis im 17. Jahrhundert, Maltechnik 89 (1983), 169-174. An English translation appeared in the Intermuseum Conservation Association Newsletter, 16 (1985), 1-6.
- 9 Gettens, R.J., Polymerized Vinyl Acetate and Related Compounds in the Restoration of Objects of Art, Technical Studies in the Field of the Fine Arts, 4 (1935/6), 15-27.
- 10 Thomson, G., Some Picture Varnishes, Studies in Conservation 3 (1957), 64-78.
- 11 Feller, R.L., Factors Affecting the Appearance of Picture Varnish, Science 125 (1957), 1143-1144.
- 12 De Witte, E., Goessens - Landrie, M., Goethals, E.J., Van Lerberghe, K., and Van Springel, C., Synthesis of an Acrylic Varnish with High Refractive Index, ICOM Committee for Conservation 6th Triennial Meeting, Ottawa 1981, no. 81/16/4.
- 13 Feller, R.L., New Solvent-Type Varnishes, in: Recent Advances in Conservation, G. Thomson ed., Butterworths, London 1963, 171-175.
- 14 Thomson, G., New Picture Varnishes, in: Recent Advances in Conservation, G. Thomson ed., Butterworths, London 1963, 176-184.
- 15 Lafontaine, R.H., Decreasing the Yellowing rate of Dammar Varnish using Antioxidants, Studies in Conservation 24(1979), 14-22.
- 16 Lafontaine, R.H., Use of Stabilizers in Varnish Formulations, ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, no.81/16/5.
- 17 Potje, K., Colour Stabilizers in Pigmented Varnish Films, in Art Conservation Training Programs Conference, State Univ. of New York College at Buffalo, Cooperstown NY 1983, 123-143.

Suppliers

Rohm and Haas Co., Philadelphia, PA 19105, U.S.A.
Union Carbide Corp., Danbury, CT 06817, U.S.A.
BASF Aktiengesellschaft, D-6700 Ludwigshafen, West Germany.
Shell Chemical Co., Houston, Texas 77251, U.S.A.

RESUME

UN REEXAMEN DES PROPRIETES DE DURABILITE DES "NYLONS SOLUBLES"

Les "nylons solubles" appliqués au revêtement de consolidation des oeuvres d'art, ont été pratiquement abandonnés. L'analyse des mécanismes de vieillissement a montré, en outre, le caractère irrémédiable des phénomènes de dégradation.

Un réexamen des mécanismes de vieillissement est actuellement engagé; il montre que ces mécanismes sont également de nature oxydative, en milieu atmosphérique à température ambiante et sous l'action de la lumière. Il est donc possible de les inhiber par introduction d'additifs de stabilisation.

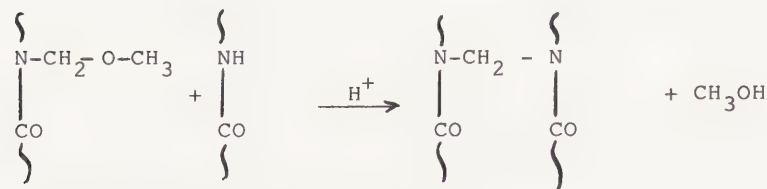
Dominique Fromageot et Jacques Lemaire

Laboratoire de Recherche des Musées de France
Palais du Louvre
75041 Paris
Cedex 01

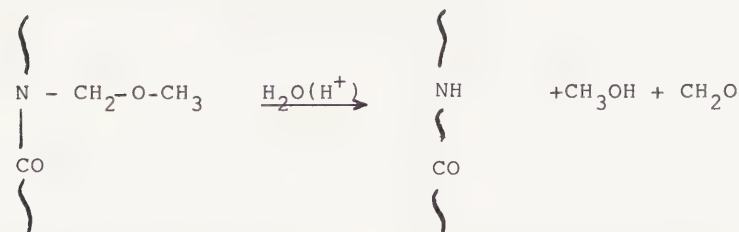
Laboratoire de Photochimie Moléculaire et
Macromoléculaire - U.A. C.N.R.S. 433 -
Université de Clermont II - Ensemble Universi-
taire de Cézeaux - B.P. 45 - 63170 Aubière

Les "nylons solubles" ont longtemps été utilisés comme revêtement protecteur "réversible" des oeuvres d'art (1 à 5). Mais les restaurateurs ont constaté que ces revêtements perdaient leurs propriétés mécaniques et devenaient insolubles à long terme sous l'influence de divers facteurs physico-chimiques. Les auteurs ont noté l'influence de la température (6), de l'eau (7) et des acides dilués sur les phénomènes d'insolubilisation. La perte de solubilité par condensation en milieu acide dilué a été mise en évidence par E. de Witte lors de l'application en surface de "nylons solubles" pour la consolidation des pierres avant opération de déssalement (7). Ce mode de vieillissement, en phase aqueuse, a été confirmé par spectrophotométrie I.R. à transformée de Fourier (6). L'insolubilisation de "nylons solubles" maintenus plusieurs mois en milieu aqueux, a été interprétée par les deux mécanismes suivants (7) :

- une réticulation chimique favorisée par les milieux acides (pH = 0,8; 1,5; 4,9; 6,1) :



- une hydrolyse des branchements :



Dans ce dernier cas, après évolution, le polymère présente des propriétés d'insolubilité analogues à celle des polyamides aliphatiques, les liaisons hydrogènes entre chaînes étant restaurées.

Lors du vieillissement atmosphérique, l'insolubilisation des revêtements de "nylons solubles" peut être interprétée par une réticulation. C'est au niveau des mécanismes de réticulation que l'analyse peut diverger. Bockhoff et coll. ont tenté de catalyser le mécanisme hydrolytique dans un "nylon soluble" exposé à l'air à 25°C et contenant de l'acide p-toluène sulfonique (6). Le vieillissement du polymère a été examiné durant trois semaines.

Ces auteurs concluent à l'intervention d'un mécanisme catalytique, bien qu'ils aient constaté que le même polymère sans catalyseur acide évolue avec une perte sensible de solubilité.

C. Sease (8) avait constaté la détérioration de revêtements de "nylons solubles" déposés sur des objets en pierre. Cet auteur a examiné l'état d'un revêtement de calaton CB déposé sur un ostracon en calcaire pendant 12 années.

Ayant interprété la perte des propriétés, en particulier l'insolubilisation, par les mécanismes proposés en 1975, C. Sease avait conclu au caractère irrémédiable de ces phénomènes et avait recommandé l'abandon des "nylons solubles". L'analyse de Bockhoff a conforté ce point de vue (6).

Le Laboratoire de Photochimie de l'Université de Clermont II examine, depuis 1979, les mécanismes de vieillissement climatique de polyamides aliphatiques (polyamide 11, 12 et 6). L'évolution chimique de ces polyamides ("vieillissement oxydant") sous l'action de la température de la lumière en présence d'oxygène et d'eau atmosphérique a été bien caractérisée (9 à 14). Or, dans tous ces phénomènes, il y a simultanément réticulation et scission de chaînes; les propriétés mécaniques et les propriétés de solubilité évoluant en fonction des événements chimiques identifiés. L'analyse de la structure moléculaire des "nylons solubles" du type polyamide substitué sur l'atome d'azote par des groupements méthylés méthoxylés, montre l'existence d'un site très privilégié situé simultanément en α de l'atome d'azote et de l'atome d'oxygène.

Il est donc apparu très vraisemblable que les variations de propriétés des polyamides solubles en vieillissement atmosphérique (température voisine de l'ambiante, éventuellement hors de l'obscurité) sont en fait les conséquences d'un vieillissement oxydant.

La présente note a pour objectif de présenter les premiers résultats d'un réexamen engagé en 1986. Ces premiers résultats semblent mettre en évidence l'intervention d'un mécanisme de réticulation oxydante. A l'opposé des mécanismes hydrolytiques très difficiles à inhiber, les mécanismes oxydatifs peuvent être profondément modifiés par l'introduction d'additifs de stabilisation thermique et photochimique. A titre d'exemple la durée de vie d'un polyamide aliphatique PA11 $[(CH_2)_{10}-CO-NH]$ est multipliée par un facteur voisin de 20 par l'introduction d'additifs photostabilisants. Ces modifications n'avaient pas été apportées jusqu'ici sur les "nylons solubles" employés en conservation, car les polymères utilisés avaient été, en fait, élaborés pour d'autres usages à court terme.

TECHNIQUES EXPERIMENTALES

1) Bases fondamentales des techniques de vieillissement accéléré

Depuis 1972, le Laboratoire de Photochimie propose de substituer aux techniques empiriques basées sur l'exposition dans les conditions naturelles ou sur l'emploi d'enceintes de simulation (Weather-o-meter, Xenotest, ...) une approche plus scientifique exploitant les techniques de photovieillissement accéléré. Cette approche respecte les principes de base suivants (état solide, film sans déficit d'oxygène, qualité de la lumière, concentration d'eau constante dans les films exposés, équilibre photo-oxydation - thermo-oxydation):

- les phénomènes de vieillissement doivent être appréhendés comme caractérisant des matériaux;
- un matériau polymère qui évolue est le siège de réactions chimiques qu'il convient d'analyser de façon détaillée. Un mécanisme d'évolution chimique qui tient compte des groupements intermédiaires et finaux, rend alors compte des modifications chimiques et permet d'interpréter les variations de propriétés physiques observées simultanément (alors qu'il n'est pas possible, dans l'état actuel de nos connaissances, de déduire une évolution chimique, d'une variation de propriétés physiques);
- l'accélération de l'évolution chimique du matériau est provoquée en laboratoire dans des conditions expérimentales qui permettent d'observer des phénomènes représentatifs de ceux qui sont impliqués dans le vieillissement naturel;
- on vérifie, en outre, à l'échelle moléculaire, que les phénomènes chimiques observés en laboratoire, dans des conditions d'accélération, sont de même nature que ceux mis en jeu dans le vieillissement naturel;
- cette vérification doit être effectuée à très faible taux d'avancement des réactions chimiques, faible taux qui peut correspondre à une détérioration complète des propriétés physiques;
- on évalue le facteur d'accélération utilisé en laboratoire par la comparaison de deux lois cinétiques de formation de photo-produits critiques en vieillissement artificiel accéléré et en vieillissement naturel pendant une phase très précoce. On peut alors prévoir la durée de vie du matériau dans les conditions naturelles.

2) Description de l'enceinte SAIREM SEPAP 12.24

Ce dispositif qui permet d'analyser les phénomènes a été décrit dans de nombreux articles (9 à 11). Nous en rappelons les éléments essentiels.

Cette enceinte est équipée de 4 lampes à arc à vapeur de mercure de type moyenne pression (Mazda MA 400 W). L'enveloppe des lampes est un filtre "solarisé" de borosilicate qui ne laisse passer que les rayonnements de longueur d'ondes supérieures à 300nm. Les échantillons sont disposés sur une tourelle cylindrique animée d'un mouvement de rotation uniforme. La tourelle peut contenir jusqu'à 24 échantillons. Elle est située au centre d'une enceinte parallélépipédique dont les 4 angles sont occupés par les quatre sources.

Le contrôle et la régulation de la température des échantillons sont assurés par une thermosonde de Platine; cette thermosonde commande par l'intermédiaire d'un "Eurotherm" des ventilateurs fixés sur les parois de l'enceinte. Ce dispositif permet de réaliser des températures constantes à 2°C près dans la plage 50-80°C.

Le support d'échantillon permet d'exercer ou non une contrainte maintenue (en général inférieure à 10% de la charge à la rupture).

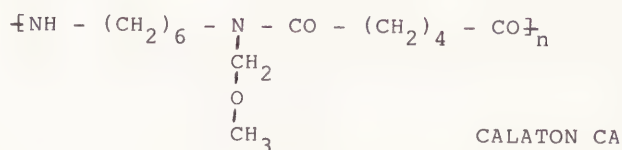
3) Déterminations spectrophotométriques

L'évolution des spectres infra-rouge des films, au cours de l'exposition, a été étudiée à l'aide d'un spectrophotomètre à transformée de Fourier, Perkin Elmer modèle 1750. Les spectres d'absorption UV-visible ont été enregistrés sur un spectrophotomètre Perkin Elmer modèle Lambda 5 équipé d'une sphère d'intégration.

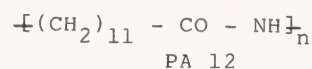
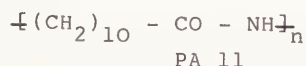
RESULTATS EXPERIMENTAUX ET DISCUSSION

- Etude comparée de la photo-oxydation à 60°C d'un "nylon soluble" et de polyamides 6 et 11

Le polymère étudié est le polyamide 6.6 modifié par des substituants méthylés méthoxylés, connu sous le nom commercial de CALATON CA (ICI).



Il a été mis sous forme de film de 10 à 60 µm d'épaisseur, par évaporation à partir d'une solution eau (25%) - éthanol (75%) préalablement chauffée à 40°C; ou pressage (6 min à 160°C). Des films d'épaisseur voisine de 40 µm ont été irradiés en enceinte SAIREM SEPAP 12.24 en parallèle avec des films de 40 µm de polyundécanoamides PA11 et de polyduodécanamide PA12 (polyamides commercialisés sous le nom de RILSAN 11 et 12 par ATOCHEM, Paris).



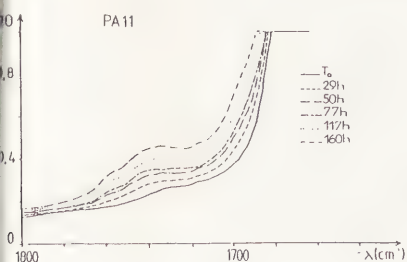


Fig. 1a

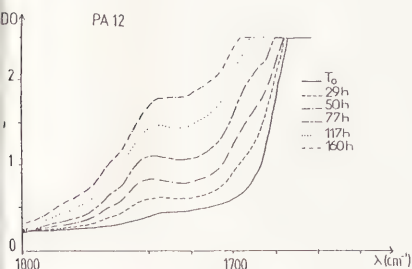


Fig. 1b

Fig. 1a et 1b : évolution des spectres d'absorption IR entre 1800 et 1650 cm^{-1} de films de polyamide 11 (a) et 12 (b) en fonction de la durée d'irradiation aux longueurs d'onde supérieures à 300 nm, à 60°C.

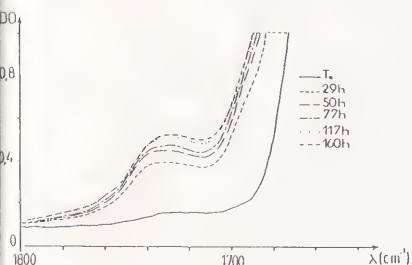


Fig. 1c

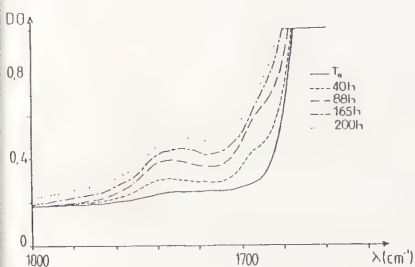


Fig. 1d

Fig. 1c et 1d : évolution des spectres d'absorption IR entre 1800 et 1650 cm^{-1} de films de calaton CA d'épaisseur de 40 μm (c) et d'épaisseur de 10 μm (d).

L'évolution des spectres I.R. des échantillons irradiés est particulièrement significative dans le domaine des carbonyles. Les spectres des échantillons de PA 11 et PA 12 (figures 1a et 1b), mettent en évidence la formation de groupement imides absorbant à 1735 cm^{-1} et à 1690 cm^{-1} ; cette deuxième bande est facilement observable dans le PA 12.

De la même façon, la photo-oxydation du CALATON CA met en évidence la formation d'imides absorbant également à 1735 cm^{-1} (figure 1c). La bande d'absorption à 1690 cm^{-1} des groupements imides est plus facilement observée sur un film de 10 μm (figure 1d). L'évolution comparée de ces différents polyamides à même degré de formation des groupements imides, montre que le CALATON CA a une absorption supplémentaire autour de 1728 cm^{-1} .

Au cours de l'irradiation de films de "nylon soluble", l'absorption des groupements carbonyles croît d'abord rapidement ($t < 100\text{h}$) puis beaucoup plus lentement et ceci quelle que soit la fréquence observée entre 1760 et 1690 cm^{-1} . Au contraire, la photo-oxydation des polyamides 11 et 12 se traduit par une augmentation de l'absorption des groupements carbonyles qui ne se ralentit pas pendant l'exposition. La figure 2 met en évidence, à 1735 cm^{-1} , ces différences de cinétiques pour les films de 40 μm d'épaisseur. La bande à 1080 cm^{-1} , attribuable aux groupement éthers présents initialement (bande qui permet de différencier le nylon soluble des polyamides non substitués), décroît au cours de l'irradiation (figure 3). La décroissance est rapide pendant les 100 premières heures d'exposition, puis on atteint une valeur pseudo-stationnaire de la densité optique à 1080 cm^{-1} . Dans l'état actuel de nos connaissances, la bande d'absorption qui se développe à 1200 cm^{-1} n'a pas été attribuée.

L'évolution des spectres U.V. des échantillons de "nylon soluble" montre qu'il ne se crée pas, au cours de la photo-oxydation, de produits provoquant un jaunissement. En cela, le "nylon soluble" se comporte comme un polyamide aliphatique PA 11.

Les échantillons de "nylon soluble" exposés en enceinte SAIREM SEPAP 12.24 ont été placés, après irradiation, dans un mélange eau+ éthanol à 40°C, milieu dans lequel le nylon étudié est initialement soluble. La dissolution de films de 30 μm d'épaisseur, dans ce milieu, est très rapide (moins de 30s).

Après 40 heures d'irradiation, les propriétés de solubilité ne sont pratiquement pas modifiées, mais après 65 heures d'exposition, on constate que les films présentent des zones insolubles dans le milieu éthanol-eau à 40°C; ils se divisent, en effet, en fragments insolubles.

Les conclusions de ce travail seront vérifiées par une analyse plus détaillée des propriétés de stabilité thermique, photo-chimique et hydrolytique des différents groupements produits dans l'oxydation. Ceci permettra d'adapter à ce matériau des techniques de stabilisation par additifs.

Remerciement

Les auteurs remercient la société ICI France de leur avoir gracieusement fourni du CALATON CA.

Références

1. H.J. Plenderleith and A.E.A. Werner, The Conservation of Antiquities and Works of Art, 2nd Edition (London : Oxford University Press, 1971).
2. O.P. Agrawal, Conservation in the Tropics, International Centre for Conservation, (New Delhi, 1974), pp. 20-29.
3. D.J. Van Dyke-Lee, "The Conservation of a preserved human head", Studies in Conservation 19, no.4 (1974) 222.226.
4. H.J. Gowers, "The Conservation of a Tlingit Blanket", Studies in Conservation 13, (1968), 98.101.
5. S. Davison, Recensement des adhésifs et consolidants utilisés pour les verres archéologiques, Adhésifs et Consolidants (Paris, IIC, 1985).
6. F. Bockhoff, Ker-Min Guo, G.E. Richards and E. Bockhoff, Etudes à l'Infra-rouge sur la Cinétique de l'Insolubilisation du Nylon Soluble, Adhésifs et Consolidants (Paris, IIC, 1984) pp83-88
7. E. de Witte, "Soluble Nylon as Consolidant Agent for Stone", Studies in Conservation 20 (1975), pp 30-34
8. C. Sease, "The Case against using Soluble Nylon in Conservation Work", Studies in Conservation 26, (1981), pp.102-110.
9. L. Tang, J. Lemaire, D. Sallet, J.M. Mery, Makromol. Chem. 182, 3467, (1981).
10. L. Tang, D. Sallet, J. Lemaire, Macromolecules 15, 1432 (1982).
11. L. Tang, D. Sallet, J. Lemaire, Macromolecules 15, 1437, (1982).
12. A. Roger, D. Sallet, J. Lemaire, Macromolecules 18, 1771, (1985).
13. A. Roger, D. Sallet, J. Lemaire, Macromolecules 19, 579, (1986).
14. A. Roger, D. Sallet, J. Lacoste, J. Lemaire, Macromol. Chem. 187, 1819, (1986).



SUMMARY

The mixture of silane and organic resin was evaluated in the laboratory as consolidant of granularly decayed stone. The evaluation was done by testing how strongly and durably the mixture fixed stone granules on a substrate stone piece. As a result, the mixture of silane solution [SS-101] and acrylic resin [Paraloid B-72] proved to be highly superior. The role of the acrylic resin Paraloid B-72, when mixed with the silane solution SS-101, is to increase the viscosity of the mixture properly so that the mixture not only penetrates but also remains sufficiently in the voids among the stone granules and the stone substrate, and to give the mixture gluing ability in the early stage which the silane by itself lacks. The high durability of the mixture after curing depends on the excellent durability of the silane.

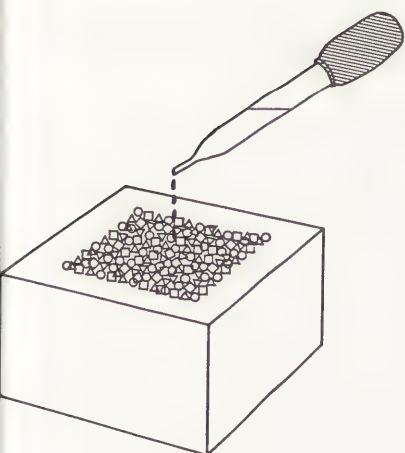


Fig. 1 Fixing of stone granules on the substrate by dropping impregnation

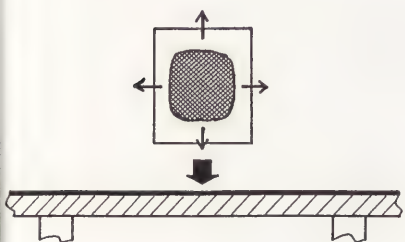


Fig. 2 Falling test

LABORATORY EVALUATION OF THE MIXTURE OF SILANE AND ORGANIC RESIN AS CONSOLIDANT OF GRANULARLY DECAYED STONE

Tadateru Nishiura

Senior Conservation Scientist

Tokyo National Research Institute of Cultural Properties

Department of Restoration Techniques

13-27 Ueno Park, Taito-ku, Tokyo, 110 Japan

Introduction

A solution of silane is suitable in consolidating powdery or chalkingly decayed stone. The solution penetrates into such a stone deeply and makes it regain its original cohesion. However, it is not so useful for granularly decayed stone, because its tackiness is too low to join stone granules and it remains a little in the voids among them. On the other hand, organic resins (epoxy, acrylic resin, etc.) have much lower durability than silane, though they have adequate tackiness and ability to remain in the voids. Thus, a mixture of silane and organic resin was considered as consolidant of granularly decayed stone. This paper describes the laboratory evaluation of the mixture as a consolidant for such a purpose.

EXPERIMENTAL

1. Test Piece

Stone granules with diameter of 1-4 mm were made by smashing a porous tuff (Oya stone). The stone granules were put on a stone piece (5×5×5cm) of the same porous tuff. Then a consolidant was impregnated into the mass of granules by dropping it onto the mass by using a syringe as shown in Fig. 1. Three test pieces were made, each for nine kinds of consolidants listed in Table 1.

2. Test Method

The test pieces were kept at room temperature for 24 hours after the consolidation treatment. Then they were put in a 50°C oven for 48 hours, so that the consolidants cured adequately. After that they were subjected to the following test:

1) Falling test

The test pieces were let fall from 2 cm high onto a hard laboratory table. This was done in all four directions, each time keeping the face on which the stone granules were fixed horizontal to the table as shown in Fig. 2.

Table 1 Consolidants for fixing of stone granules

Consolidants	Combination of resins and solvents (wt. %)					
	E	A	S	T	C ₁	C ₂
ET	45			55		
ETC ₁	45			54	1	
ES	45		55			
ESC ₁	45		54		1	
AT		18		82		
ATC ₂		18		81		1
AS		18	82			
ASC ₂		18	81			1
S			100			

E : Epoxy resin, Araldite CY230 + Epomate B-002 [5:2]

A : Acrylic resin, Paraloid B-72

S : Silane (solution of an oligomer of methyl tri-ethoxy silane in a mixture of toluene and methanol [9:1]; silica content 28%), SS-101 (added 4% Catalyst C)

T : Toluene

C : Silane coupling agent [N-β(aminoethyl)γ-aminopropyl methyl di-methoxy silane], Shinetsu KBM-603

C : Silane coupling agent [γ-methacryloxy propyl tri-methoxy silane], Shinetsu KBM-503

2) Rubbing test I

The faces of the test pieces, on which the stone granules were fixed, were rubbed by a plastic brush and then by a wire brush.

3) Accelerated deterioration test I

The test pieces were boiled in water for 4 hours, then freeze-dried at -20°C for 18 hours, then dried in a 105°C oven for 4 hours.

4) Rubbing test II

Same as Rubbing test I.

5) Accelerated deterioration test II

The test pieces were boiled in water for 1.5 hours then continuously immersed in water for 18 hours. Then they were wrapped tightly with a polyethylene film, and were put in a freeze-thaw cyclic chamber and subjected to 17 cycles of -30°C to $+30^{\circ}\text{C}$.

5) Rubbing test III

After Test(5), the test pieces were dried in a 105°C oven for 4 hours. Then they were subjected to a rubbing test in the same way as Rubbing test I.

3. Test Results

3.1 Fixing Effect

The residual ratio of the stone granules on the substrate stone after each test is shown in Table 2.

3.2 Appearance

Before the tests, when the consolidants cured, the treated parts of the test pieces showed wet-color. And they also had gloss except for [S]. [ES] and [ESC₁] were somewhat whitened, though the degree of gloss was smaller than on the others. However, the wet-color, the gloss and the whitening disappeared after the accelerated deterioration test I, so that the treated parts of all the test pieces showed the same color and texture as their substrate stone. By the freeze-thaw cyclic treatment of the accelerated deterioration test II, cracking occurred on the substrate stone of all the test pieces but no cracks occurred on the consolidated granules and the interface between the granules and the substrate. Fig. 3 shows the condition of the test piece [AS] before and after all the tests. It shows that the wet-color and the gloss gained by the consolidation disappeared and that there was no crack on the consolidated granules after the tests.

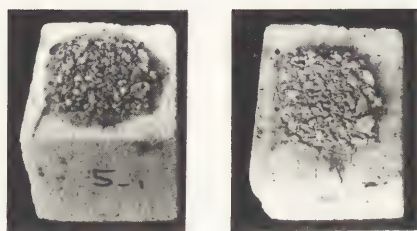


Fig. 3 Before(left) and after(right) the tests [AS]

Table 2 Residual ratio of stone granules on the substrate stone after each step of the tests

Tests \ Consolidants	ET	ETC ₁	ES	ESC ₁	AT	ATC ₂	AS	ASC ₂	S
Before tests (24 hrs. after consolidation)	100	100	100	100	100	100	100	100	90
Falling test	100	100	100	100	100	100	100	100	50
Rubbing test I (plastic brush)	100	100	100	100	100	100	100	100	40
Rubbing test I (wire brush)	95	95	100	100	100	100	100	100	10
Accelerated deterioration test I (after boiling)	95	95	100	100	10	10	100	100	10
Accelerated deterioration test I (after drying)	95	95	100	100	10	10	100	100	10
Rubbing test II (plastic brush)	90	90	95	100	5	5	100	100	5
Rubbing test II (wire brush)	50	90	95	100	0	0	100	100	0
Accelerated deterioration test II (after boiling)	50	90	95	100			100	100	
Accelerated deterioration test II (after freeze-thaw)	50	90	95	100			100	100	
Rubbing test III (plastic brush)	40	90	90	100			100	100	
Rubbing test III (wire brush)	20	80	80	100			100	100	

Percentage by eye-measurement

Discussion

The experiment proved the following facts:

1. The silane solution (SS-101), which is usually employed for consolidation of stone in Japan, can not fix stone granules. This is because its viscosity is too low to remain in the voids among the granules and it has low gluing ability in the early stage.
2. A solution of epoxy (Araldite CY230) and of acrylic resin (Paraloid B-72), whose viscosity can be optionally controlled and whose gluing ability in the early stage is high, fix the stone granules quite well. But the durability of these resins is low.
3. The mixture of the silane solution and the epoxy or the acrylic resin fixes the granules well, and its durability is high. In particular, the mixture of the silane solution and the acrylic resin is excellent, as is clearly shown in Table 2 as the difference between [AT] and [AS], and between [ATC₂] and [ASC₂].

Paraloid B-72 used in this experiment is a glassy pellet with a diameter of 3-5 mm which is applied as a solution in an organic solvent. One of the biggest merits of Paraloid B-72 is that it has high gluing ability in the early stage. But the viscosity of a solution of Paraloid B-72 is so high that, unlike epoxy, the solution of high concentration can hardly be gotten. So, when we apply a solution of Paraloid B-72 as consolidant of properly low viscosity for stone, its concentration is inevitably low, particularly compared with that of epoxy (see Table 1). This seems to be the reason for the big difference in durability between [AT]•[ATC₂] and [ET]•[ETC₁] (see Table 2). On the contrary, this characteristic of Paraloid B-72 is a big merit when mixed with the silane solution SS-101. The mixing ratio of Paraloid B-72 to SS-101 was about 2/8 (see Table 1). Since the content of final solid resin in SS-101 is about 35%, the mixing ratio of Paraloid B-72 to the solid resin of SS-101 was 2/3. On the other hand, the mixing ratio of the epoxy Araldite CY230 to the solid resin of SS-101 was about 7/3. So the content of the silane in the mixture of Paraloid B-72 and SS-101 is much higher than the mixture of Araldite CY230 and SS-101. This seems to be the reason why the mixture of Paraloid B-72 and SS-101 [AS] is more durable than the mixture of Araldite CY230 and SS-101 [ES] (see Table 2).

The role of the acrylic resin Paraloid B-72, when mixed with the silane solution SS-101, is to properly increase the viscosity of the mixture so that it can remain in the voids among the stone granules and the stone substrate and to give it gluing ability in the early stage. After curing, the durability of the mixture depends on the high durability of the silane. This is explained by the following mechanism:

When mixed with the silane solution SS-101, Paraloid B-72 does not react with the silane but is dissolved by force in the organic solvent (toluene & methanol, 9:1) in which the silane is solved. So, in the early stage of the volatilization of the solvent in the mixture, Paraloid B-72 gives the mixture high tackiness by which stone granules are joined with one another and to the substrate stone. Supported by the gelled Paraloid B-72, in the voids among stone granules and the stone substrate, the silane cures gradually. Finally when the silane cures adequately, it fixes the stone granules very strongly. The fixing lasts very long because of the high durability of the silane.

Regarding the effect of silane coupling agent, there is significant difference in durability between [ET] and [ETC₁] and between [ES] and [ESC₁], but no difference between [AT] and [ATC₂], or between [AS] and [ASC₂] (see Table 2). Therefore, as far as this experiment is concerned, it can be said that silane coupling agent is effective for epoxy but not for acrylic resin. The application of silane coupling agent for the conservation treatment of stone is an important subject for our future study.



SUMMARY

The author presents a preliminary discussion of a research project on Resin Coatings currently underway at the National Gallery of Canada, Ottawa. The proposal includes the documentation of the use of resin coatings on oil paintings in the National Gallery collections and the characterization of the naturally-aged coatings in terms of optical properties and ease of removal. The project is intended to provide information on the aging properties of naturally-aged resin coatings, applied to oil paintings which have been exposed to "ordinary gallery conditions" since the time of varnishing. The main resins to be examined in this context are synthetic thermoplastic resins including poly(butyl methacrylates) (mainly Lucite 44), Acryloid B-72 and Ketone Resin N. The results of this project will be compared with the expected aging properties predicted by published research involving other naturally-aged sample testing and accelerated-aging tests.

AN INVESTIGATION INTO RESIN COATINGS: A STUDY OF NATURALLY-AGED EXAMPLES

Barbara A. Ramsay-Jolicoeur
Conservator of Fine Art
Restoration and Conservation Laboratory
National Gallery of Canada
Ottawa, Canada K1A 0M8

Introduction

Resin varnishes are used as protective coatings during the conservation treatment of most oil paintings. Traditionally, natural resins such as damar or mastic have been employed. However, with the introduction of synthetic thermoplastic resins in the twentieth century, the natural resins have met with serious competition in the context of paintings conservation.

A range of synthetic polymers have been introduced as picture varnishes since the 1930's, in the hopes of finding a suitable coating for paintings. Resins are sought which will satisfy many requirements, including acceptable optical properties and chemical stability allowing ease of removal. Over the years, these synthetic resins have been tested, promoted, employed by conservators for a period of time and then, in most cases, abandoned in favour of more stable materials. The cycle continues, with resins being adopted and then rejected on the basis of results of scientific study and/or observations in practice.

Ongoing scientific research provides essential information used in evaluating and characterizing synthetic resins as surface coatings. Most research to date has incorporated accelerated-aging tests to generate data on the estimated aging properties of resin coatings. Very little has so far been documented as to the properties of naturally-aged examples of resin varnishes.¹

Further comparisons of naturally-aged examples with accelerated-aging test samples is very much needed in order to correlate expected and actual aging properties of resins which have been applied to oil paintings. This information could be used to assess the practical application of accelerated-aging tests; it would also be important in determining future treatment of paintings already varnished with since-abandoned synthetic resins.

Background to the Research Project

This project began several years ago as a survey of the resin coatings which had been applied to paintings in the collections of the National Gallery of Canada. Information was compiled from conservation files in the Restoration and Conservation Laboratory (RCL) where detailed records have been maintained for many decades, but particularly from 1958 onwards.

It soon became obvious that a large bank of technical information lay waiting to be discovered and studied. Of particular interest was the historical use of resin coatings. More importantly, there existed the possibility of studying the appearance and properties of these specified coatings after a documented period of natural-aging under "ordinary gallery conditions".² The concentration of technical information in RCL, coupled with a record of the display history, as well as accessibility of the paintings for study, provide a rare and valuable sampling of naturally-aged specimens.

The following paper outlines the proposal for the Resin Coating Research Project, conceived in response to a perceived need to characterize and evaluate naturally-aged resin coatings, with a view toward the practical implications for paintings conservation.

Purpose of the Research Project

The project will attempt to study, characterize and evaluate the naturally-aged resin coatings which have been applied to paintings in the National Gallery of Canada collections since the late 1950's. The resultant information will then be compared with other related research which has previously been published.

Phases of the Research Project

The project, as envisaged at this time, is divided into six (6) phases:

Phase I: Collection of Technical Information

This phase consists of the collection and compilation of technical information on specified resin coatings as documented in the conservation records of the Restoration and Conservation Laboratory. Resin type, solvent, date and method of application have usually been indicated. Many records include details such as the concentration of resin used, the presence of additives, if any, in addition to treatments undertaken prior to and subsequent to varnish application. A sample form for documenting the resin coating information is illustrated in Figure 1.

Figure 1: Sample Form for Documenting Resin Coating Information

<u>RCL RESIN COATING SURVEY</u>						R <u>24</u>
Attribution:	BELL-SMITH, Frederick M. (1846-1932)					
Title:	Daybreak					
Technique:	Oil on canvas					
Accession Number:	14,983					
Location:	5R23A					
 <u>RESIN COATING DATA</u>						
<u>Resin</u>	<u>Solvent</u>	<u>Conc.ⁿ</u>	<u>Date applied</u>	<u>Previous observations</u>	<u>Other</u>	
LUCITE 44	xylene	1:7	November 1969	Varnished after surface-cleaning with 10% sodium perborate, varnish removal with diacetone alcohol and Shellsol (2:1), and wax-resin lining. (1969)		
"two thin coatings sprayed on"						
 <u>INPAINTING DATA</u>						
N/A						
Date <u>October 11, 1982</u>			<u>BAR</u>			

As of March 1987, documentation has been collected on the resin coatings applied to 397 oil paintings, 346 of which had been varnished with synthetic thermoplastic resins since 1958. Of the latter, the following resins figure most prominently:

Lucite 44 and other, unspecified poly(butyl methacrylates): noted for 199 varnished paintings;

Acryloid B-72: noted for 84 varnished paintings;

Ketone Resin N: noted for 22 varnished paintings.

Other documented resin types include various poly(vinyl acetates), Resin AW-2, Acryloid B-67, as well as the natural resin, damar.

Figures 2 - 6 illustrate the distribution of different resins used over the period 1958 through 1984. It can be noted that many of the poly(butyl methacrylate) coatings have aged naturally for 20 to 29 years (Figures 3 and 4).

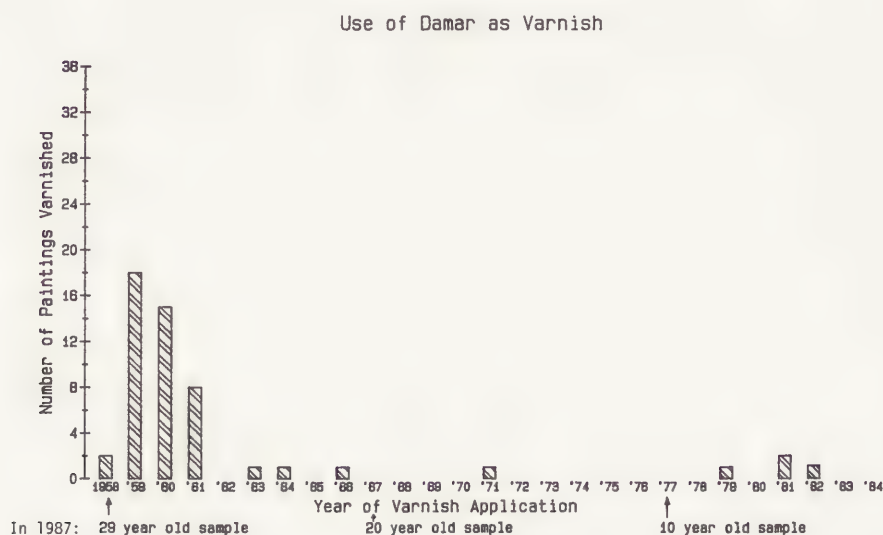


Figure 2. Use of Damar as Varnish in Documented Paintings

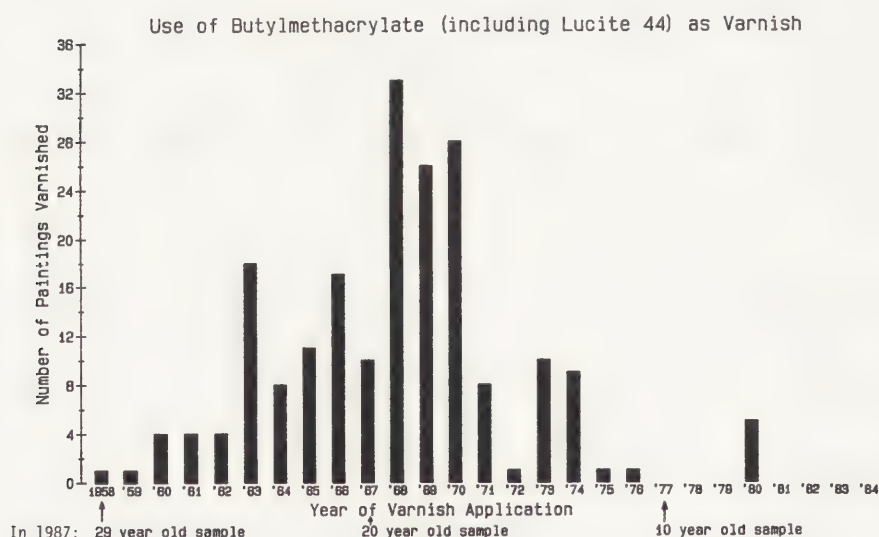


Figure 3. Use of Butylmethacrylate (including Lucite 44) as Varnish in Documented Paintings

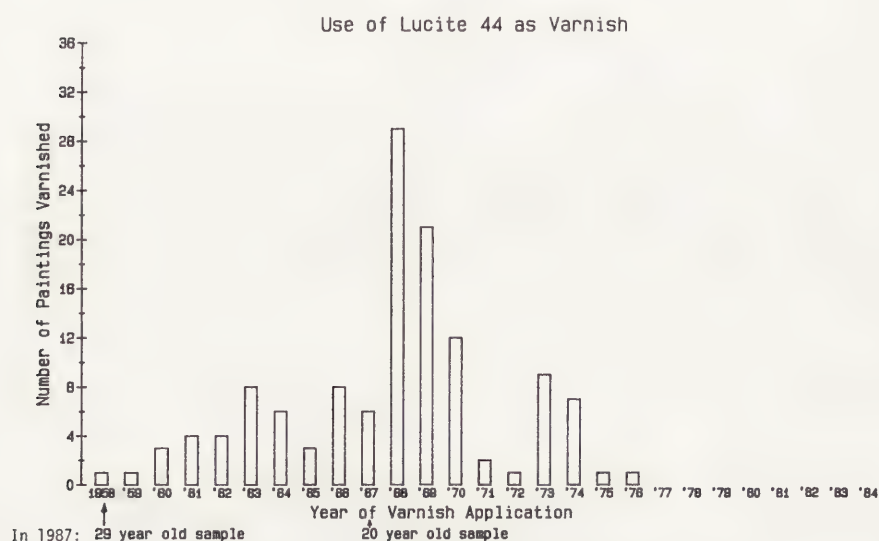


Figure 4. Use of Lucite 44 as Varnish in Documented Paintings

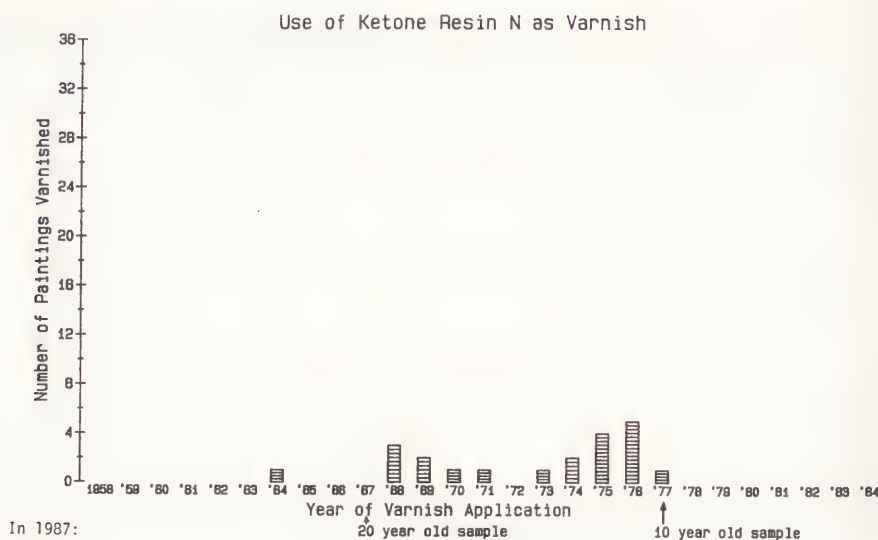


Figure 5. Use of Ketone Resin N as Varnish in Documented Paintings

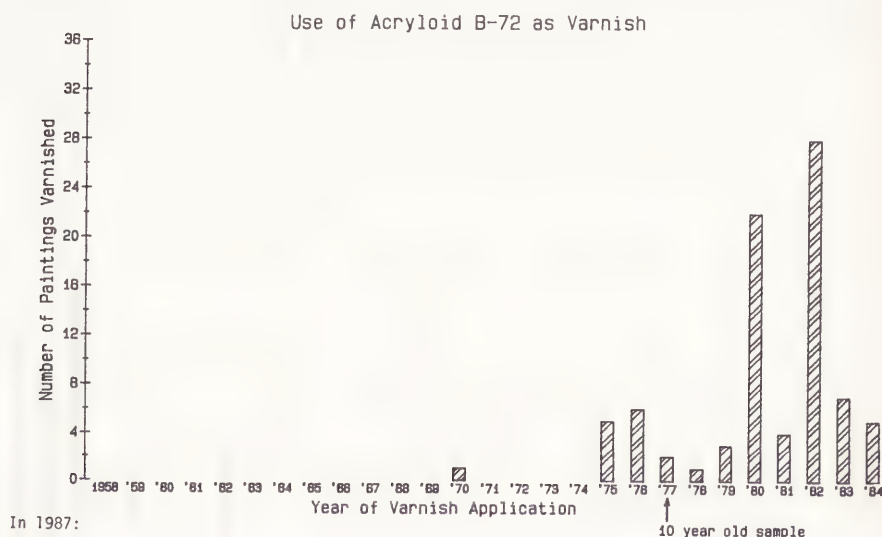


Figure 6. Use of Acryloid B-72 as Varnish in Documented Paintings

This data-collecting phase of the project will have been completed by the time of the ICOM Committee for Conservation Meetings in Sydney. It is hoped that computerization of the data will also have been implemented by that time.

Phase II: Examination and Characterization of the Resin Coatings

Further study will focus on the paintings which fall into categories based on the type of resin coating applied. Figures 3 and 4 indicate that the large sampling of paintings coated with **poly(butyl methacrylate)** provides a logical starting point for characterization and evaluation. These resins have already undergone considerable study³⁻⁹ and will therefore have much data with which to compare. They are also important resins to investigate due to repeated warnings concerning their increased insolubility upon aging.

Paintings coated with **Ketone Resin N** also warrant attention due to the concern expressed in recent years with respect to the increased insolubility of this resin with age.^{10,11} Although not a large sampling in the National Gallery collections, the coatings on these paintings will be assessed in terms of their aging properties. (Figure 5)

The larger sampling of paintings coated with **Acryloid B-72** has been treated more recently and, due to perceived stability of this resin, does not require immediate study. Future evaluation could be carried out with the data thus compiled (Figure 6).

In this phase, it is intended that the paintings in each category of resin type will be examined and the coatings will be characterized on the basis of their colour, transparency, gloss, surface texture, craquelure and perhaps other standard tests. A preliminary survey of the paintings in question will determine to some extent which properties will be most relevant for this study. Suitable test methods, both quantitative and subjective, will be employed. This information will be used to evaluate the optical properties of the aged resin coatings.

Phase III: Solubility Testing of the Resin Coatings

The next phase will involve the systematic testing of the solubility of the naturally-aged resin coatings. In collaboration with the Canadian Conservation Institute, standardized test procedures involving solvent-swab tests, and possibly solvent-droplet tests, will be applied. Observations will be made on the ease of removal, as well as general removal behaviour, of the resin coatings during the solubility testing procedure.

The practical implications of these tests may include determination of the need to remove from paintings resin coatings which are becoming obviously more insoluble. It is conceivable that different stages in solubility may be observable in paintings varnished at different times and/or exposed to different conditions prior to or subsequent to varnishing.

Phase IV: Analysis of the Resin Coatings

As a follow-up to the Solubility Testing Phase of the project, samples of the removed resin will be analyzed to confirm their classification type. The assistance of the Canadian Conservation Institute will be requested for this stage.

As a sideline to this project, samples of the naturally-aged resin coatings will be provided to E. DeWitte, Institut Royal du Patrimoine Artistique, for inclusion in his ongoing research into identification of the degradation products present in aged resin coatings.¹²

Phase V: Observations, Interpretation and Conclusions

This phase will involve the careful examination of data collected and the determination of any trends or patterns in the solubility or changes in appearance of the resin coatings. Conclusions will be drawn concerning the actual aging properties of the naturally-aged examples. These will be compared with the data of other, published research, particularly that arising from accelerated-aging test procedures. Positive and negative correlations will be noted.

Phase VI: Publication

The results of this research project will be disseminated in published form at reasonable intervals via suitable channels.

It is anticipated that there will be results of this research project in time for the ICOM Committee for Conservation Meetings of 1990.

Conclusion

The purpose of presenting the proposal and status of this research project is to bring to the attention of readers the type of work which, at this time, is planned, to seek comments and advice from my professional colleagues and to encourage others in similar museum situations to compile documentation on resin coatings which may form part of future studies.

The author acknowledges that specific problems are inherent in undertaking such a research project, involving the testing of real works of art instead of standardized test samples. Certain constraints and limitations will inevitably be imposed concerning the testing and interpretation of the results, due to the range of variables involved. It is hoped, however, that this study will contribute to the existing knowledge of the degradation processes occurring in synthetic resin coatings, and that it will provide information useful to conservators involved in the practice of paintings conservation.

It is also appreciated that the realization of this ambitious project will only be possible with the continued cooperation of the staff of the National Gallery of Canada, the Canadian Conservation Institute, and other colleagues who may offer their interest, assistance and support.

References and Notes

- 1 A notable exception is the work done on varnished test panels at the Fogg Art Museum, Boston. These panels, coated with a range of varnishes in the late 1930's, have been tested for solvent removal by the National Gallery of Art Research Project, Mellon Institute, and provide some of the oldest identified naturally-aged varnish specimens available. In addition, paper chromatography procedures have been applied at the National Gallery, London, by Thomson and at the Mellon Institute, in the testing of the solubility of varnish applied to actual painting surfaces. (Feller, R.L., Stolow, N. and E.H. Jones, On Picture Varnishes and Their Solvents, Revised and Enlarged Edition, Washington D.C.: National Gallery of Art, 1985 (pp. 158-160, 171, 196, 197, 200).
- 2 By this term is meant conditions of a controlled museum environment where, in storage or on display, the varnished paintings have not been deliberately subjected to extremes of temperature or relative humidity or to excessive light exposure. This is in marked contrast to the accelerated-aging test conditions in which high temperatures and/or high levels of light exposure are involved.
- 3 Feller, R.L. "Crosslinking of Methacrylate Polymers by Ultra-violet Radiation" in Papers Presented at the New York Meeting, Division of Paint, Plastics and Printing Ink Chemistry, American Chemical Society, vol. 17, No. 2 (September 1957) pp. 465-470.
- 4 Feller, R.L. "Early Studies on the Cross-linking of Methacrylate Polymers" (Appendix A) in Feller, R.L., Stolow, N. and E.H. Jones, On Picture Varnishes and Their Solvents, Revised and Enlarged Edition, Washington, D.C.: National Gallery of Art, 1985 (pp. 195-201).
- 5 Feller, R.L. "Studies of the Effect of Light on Protective Coatings Using Aluminum Foil as a Support: Determination of Ratio of Chain Breaking to Cross-linking" (Appendix C) in Feller, R.L., Stolow, N. and E.H. Jones, On Picture Varnishes and Their Solvents, Revised and Enlarged Edition, Washington, D.C.: National Gallery of Art, 1985 (pp. 211-217).
- 6 Feller, R.L. "Properties of a Mature Varnish" in Feller, R.L., Stolow, N. and E.H. Jones, On Picture Varnishes and Their Solvents, Revised and Enlarged Edition, Washington, D.C.: National Gallery of Art, 1985 (pp. 146-167).
- 7 Feller, R.L. "Studies in the Photochemical Stability of Thermoplastic Resins" in ICOM Committee for Conservation Preprints: Fourth Triennial Meeting (Venice 1975) Paper 75/22/4 (pp. 5,6).
- 8 Feller, R.L. "The Relative Solvent Power Needed to Remove Various Aged Solvent-Type Coatings" in Conservation and Restoration of Pictorial Art, London: Butterworths, 1976 (Table 22.2; p. 160).
- 9 Feller, R.L. "Thermoplastic Polymers Currently in Use as Protective Coatings and Potential Directions for Further Research" in Bulletin of the Institute for the Conservation of Cultural Material (ICCM), vol. 10, No. 2 (1984) pp. 5-18.

- 10 Feller, R.L. and M. Curran, "Changes in Solubility and Removability of Varnish Resins with Age" in Bulletin of the American Institute for Conservation, vol. 15, No. 2 (Summer 1975) pp. 17-26.
- 11 Lafontaine, R.H., "The Effect of Inhibitors on the Removability of Aged Ketone Resin N Varnish Films" in Journal of the International Institute for Conservation - Canadian Group (IIC-CG), vol. 3, No. 2 (Spring 1978) pp. 7-12.
- 12 Personal communication from E. DeWitte, Institut Royal du Patrimoine Artistique, Bruxelles (April 11, 1984).

Figures

- Figure 1:** Sample Form For Documenting Resin Coating Information
- Figure 2:** Use of Damar as Varnish in Documented Paintings
- Figure 3:** Use of Butylmethacrylate (including Lucite 44) as Varnish in Documented Paintings
- Figure 4:** Use of Lucite 44 as Varnish in Documented Paintings
- Figure 5:** Use of Ketone Resin N as Varnish in Documented Paintings
- Figure 6:** Use of Acryloid B-72 as Varnish in Documented Paintings

Materials

- Lucite 44:** poly(n-butyl methacrylate) resin; previously manufactured by Dupont; replaced by Elvacite 2044.
- Acryloid B-72:** ethyl methacrylate/ methyl acrylate copolymer; manufactured by Rohm and Haas, U.S.A. ("Paraloid" B-72 is by Rohm and Haas, Germany).
- Ketone Resin N:** poly(cyclohexanone) resin; previously manufactured by Badische Anilin & Soda Fabrik (BASF), Germany; replaced by Laropal K 80.
- Resin AW-2:** resin based on poly(cyclohexanone); previously manufactured by Badische Anilin & Soda Fabrik (BASF), Germany.
- Acryloid B-67:** poly(isobutyl methacrylate) resin; manufactured by Rohm and Haas, U.S.A. ("Paraloid" B-67 is by Rohm and Haas, Germany).



SUMMARY

What started as a request to find the secret of the Italian violin makers became a research into the possibilities and limits to analyse complex varnish mixtures at all.

Testing well tried analytical methods against self prepared and thus known sample material it was found that even with a large sample the identification of all the ingredients of a mixture is difficult, if not impossible. The main components in each recipe could be definitely identified. However, in order to carry out as thorough an analysis of the mixture as possible at least three analytical methods had to be used.

RESEARCH ON THE ANALYSIS OF VARNISH MIXTURES AS USED ON OLD BOWED INSTRUMENTS: POSSIBILITIES AND LIMITS

Wilma G.Th. Roelofs, Riet F.S. Karreman, Judith H. Hofenk de Graaff
Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam, The Netherlands

Introduction

A veritable "mer a boire" of literature exists concerning the "secret" of the Italian violin makers such as Amati, Stradivarius, and Guarneri. (2,3,5,17,18,19,27,31,37,38,44,46,54,55). These violins have been subjected to thorough examinations of every part. The type of wood, its thickness, the violin's construction, wood pre-treatments, types of varnish, etc., have all been studied. Violin makers, together with scientists, have attempted to recreate these instruments and their magnificent tones (6, 9, 28, 42, 58).

There has been much speculation about the treatment of the wood, the priming used, and the formulation and make-up of the veneer, all of which are responsible for a violin's tone (11, 14, 33). Many recipes have been given with the claim to be "The varnish" used by the Italian violin makers (10, 12, 28, 33, 36, 48). There are at least dozens, if not hundreds, of different recipes which vary greatly in formulation.

Combinations of natural resins, such as colophony, dammar, Venice turpentine, etc., and of oils, are included. (22,26,49). The use of propolis* has been the subject of many discussions. There are also different opinions about the number of varnish layers applied to the instruments, from 5 to 15 layers.

A proper understanding of these problems is not only of importance in establishing the age and/or authenticity of an instrument. It could also add a new dimension to what is known about the craft of making bowed instruments.

For years now, the Central Research Laboratory for Objects of Art and Science has been engaged in the analysis of the structure and composition of paint and varnish layers on objects of art.

Because of this experience, the Central Research Laboratory was approached by the late H. Eskes, a violin collector from Apeldoorn, Netherlands and the violinmaker A. Pisters, from Schin op Geul, Netherlands, with the request to analyse the composition and structure of varnish used on Italian bowed instruments from the 16th to the 18th century.

For the analysis of resins and the structure of the varnish layers, small samples from accurately dated instruments were made available.

During previous analyses of varnish samples from a few 18th century violins, two different resin types were identified.

Since the samples were very small (<1 mm²), it was not clear whether or not there were actually more resins present in less than detectable amounts.

To find out whether or not commonly used analytical methods, such as microscopy, infrared spectroscopy and thin layer chromatography, are suitable for the purpose mentioned above, we needed larger samples with known ingredients.

This was important for a number of reasons.

- Because of the problems in the research on mixtures of resins.
- The need for use of different analytical methods.
- To check the correctness of analytical methods on known ingredients.
- To make it possible in a later stage of this project to imitate the ageing process, in order to check for changes which may have occurred in the varnish.

An extensive literature review was carried out on recipes which have been used in the past. A number of representative combination were chosen, and these were applied to test boards. Samples taken from these test boards were then examined for their composition and structure, using the research methods listed above.

* Propolis bee bread, hive dross. A resinous substance found in beehives. Collected by bees from buds. Propolis balsam has a hyacinth odour and is said to contain 10% cinnamyl alcohol. (4, 13, 16, 29, 56, 57)

Choice of recipes

- A large amount of literature exists on the topic of varnishes for bowed instruments.
- This literature was put together and investigated by H. Eskes.
- In 1927, Altmann (43) made a chronological review of publications from the 19th and early 20th centuries which included more than 150 titles. On these, Mailand and Niederheitmann are of particular importance (33, 43). Sacconi, Michelman and Thompson, among others, are most important among the more recent publications (36, 48, 52, 53).
- Together with A. Pisters, 8 documented recipes were chosen for the investigation described here, along with two recipes of their own. The eight documented recipes were chosen from Fulton, Sacconi, and Mailand (12, 52, 53, 48, 36), to represent those most frequently cited.
- The recipes can be divided into a few of groups, e.g., oil varnishes and spirit varnishes. These groups, in turn, can be divided according to resin, such as mastic, sandarac, dammar, etc., and by oil, such as linseed oil, eucalyptus oil, spike oil, etc.* There are also various additives such as natural dyes. Test boards were made with the chosen recipes.

Preparation on the test boards

The basic material for the test boards was 3 mm thick maple or whitewood. These are the kinds of wood most often used for making bowed instruments. Layers were applied to the boards so that with each new layer, an area remained untreated. This meant that a board treated with 8 layers was comprised of 8 sections which had 1, 2, 3,, 8 varnish layers, respectively. In this way, it was possible to check whether the structure of the layers could be analyzed correctly.

Analytical methods

The following methods were used for the analysis of the test boards:

- microscopy
- infrared spectroscopy
- thin layer chromatography.

Examinations on recipe B

From the test boards which had been prepared, the one with recipe B was chosen for the preliminary work. The reason for this choice was twofold:

- The varnish was the most uniform and was not cracked. This was especially important for the microscopic work.
- The formulation was not too complex. This was an advantage in the analysis of the raw materials used, because it reduces the number of variables.

The materials used for the preparation of recipe B, viz. colophony, heated colophony, crude linseed oil, gum turpentine, twice boiled linseed oil, and alizarin, were analyzed beforehand using infrared spectroscopy and thin layer chromatography. This was necessary in order to determine the specific absorption peaks in the infrared spectrum, and Rf values of the various components in the chromatogram.

When natural substances are being used, it is important to know about the variations which can occur in them. Natural products are often polluted with by-products, and each delivery may be different. When identifying an unknown sample, it is therefore important to determine the main component which is specific to each substance.

Microscopy (1, 15, 35)

Samples were taken from layers 1 through 7 of board B, using a binocular microscope (magnification 8X - 40X) and lancet. These samples were ca. 1 - 2 mm² in size, and contained the layers of varnish and a small piece of wood. The samples were embedded in polyester resin (Poly-pol type PS 230). After hardening the cross sections were wet-ground with fine sandpaper and then polished

* For the origin and composition of the materials mentioned here see L. Masschelein-Kleiner, Ancient binding media, varnishes and adhesives. Rome, 1985.

with a suspension of aluminium oxide. The cross sections were studied under a microscope. An Orthoplan Microscope (Leitz) with a magnification range of 200X - 800X was used for the examinations. These examinations included the use of reflected light, polarized light and techniques of ultraviolet fluorescence.

Problems with the embedding and grinding of the samples

Problems arose during the grinding of the embedded samples, due to the freshness layers of the varnish. This would be less of a problem with samples from old instruments, where the layers of varnish have hardened much more thoroughly. Also, any remainder of wood in the sample was made as thin as possible before the sample was embedded in order to reduce the effect of swelling.

When the cross-sections were examined under the microscope, it turned out to be very difficult to differentiate between the varnish layers and the embedding compound, because both were transparent. The problem was solved by the use of a blue coloured embedding compound (Polyester blue pigment paste). This resulted in a clear distinction between the embedding material and the embedded varnish layers.

Problems with the microscopic analysis

Often, more layers were counted in a section than actually were there. This was caused by reflections on curved parts of the surface of the cross section and other optical phenomena. These phenomena also occurred at interfaces with the embedding compound.

When there was no grinding between two varnish layers, it was very difficult to differentiate between them, although in some cases it was possible to make this distinction if an extra colour had been added to the varnish. Due to the relatively short period of time that the layers were allowed to dry between applications, diffusion amongst them may have occurred. In addition, the composition of the layers was identical, resulting in no differences in fluorescence. A clear distinction between the layers was, in most cases, only visible when the varnish had been ground between the application of layers.

Conclusion

Using the methods described above for embedding, grinding and microscopic analysis, it is not possible to determine the number of layers which has been applied. This is the result of a number of factors:

- Diffusion occurs between layers which are not ground before a new layer of varnish is applied.
- Layers are disturbed by the grinding when the cross-sections are made, and become filled with polishing powder.
- Reflections occur, causing errors in the interpretation of the number of layers present.

Analysis of the materials used

Prior to the actual analysis of the samples taken from board B, the materials used for the preparation of recipe B were analyzed separately. These were:

- colophony
- colophony, heated 12 hours at 250°C
- crude linseed oil
- crude linseed oil, heated to 300°C
- twice boiled linseed oil
- gum turpentine
- alizarin.

Infrared spectroscopy - IR - (8, 23, 24, 25, 30, 32)

In order to make the infrared spectrum, the materials were mixed with potassium bromide and pressed into a pellet 13 mm in diam. The spectrum was registered by a Perkin-Elmer infrared spectrophotometer, model no. 377.

Results

Between the spectra of crude linseed oil, linseed oil heated to 300°C and linseed oil which has been boiled twice, no significant differences appear. It is thus not possible to identify mixtures of these substances using IR. When colophony is heated to 250°C, it

gains a peak at 1570 cm^{-1} , but loses one at 1280 cm^{-1} . In theory, it should be possible to identify both unheated and heated colophony in mixtures.

No difference can be shown between gum turpentine and colophony, though. Using IR, it is possible to show whether a mixture contains an oil, resin, or wax, but in most cases not the particular type. Identification is only possible when the concentration of one of the substances in the mixture is high enough. Ethereal oils, such as eucalyptus oil or spike oil, cannot be identified in a mixture containing a resin, because the important peaks of both overlap.

Thin layer chromatography - TLC - (20, 21, 34, 41, 45, 47, 51)

The method of separation described by Roelofs (47) was chosen for the analysis of resins. Oils, such as those which appear in the recipe, cannot be identified using this method of separation. As it is possible, however, that these oils interfere with the identification of resins when using TLC, the method of separation was checked by testing it in the presence of oils. This check was carried out for alizarin and asphaltum for the same reason. Oils can be analyzed using gas chromatography (39, 40, 59, 60). It is also possible to carry out a steroid test with thin layer chromatography to confirm the presence of oils and, with an adequate sample, also the type of oil (7). For a steroid test, however, a larger sample is required than for gas chromatography.

Results

There is a difference between the individual thin layer chromatograms of colophony and heated colophony. During the heating of colophony, a chemical reaction takes place the product of which appears in the chromatogram as a fluorescent tailing spot. Still, when a mixture contains both of these substances, no distinction can be made between them. This is because when low concentrations are involved, the main component used for identification purposes remains the same for both substances. Fresh gum turpentine has a clearly different chromatogram from colophony and thus should be identifiable in a mixture. The problem is, however, that fresh gum turpentine contains colophony as well as turpentine oil. When the varnish dries, a change takes place. The oil becomes resinous (polymerizes) so that gum turpentine mixed with colophony can no longer be differentiated from the pure resin colophony. The method of separation for resins is not at the same time optimal for the separation of oils, alizarin and asphaltum. Although, it can still be used to indicate the presence of substances, with the exception of twice boiled oil, when the concentrations are sufficiently high. In a mixture including resins, the identification of the above mentioned substances will cause problems. The R_f values of the various components are often the same as those of the resins, thus causing a "haziness" of the chromatogram. The concentrations are too low and thus the most important components which are to be identified are not visible.

If oils, alizarin, and asphaltum must all be identified positively from a mixture, an extra chromatographic separation system is required. Gas chromatography (39, 40) or a steroid test can be used for the analysis of oils. For alizarin and possibly other red dyes, TLC can be used (20, 21).

These considerations result in the conclusion that in the case of complicated mixtures of resins, oils and dyes, several analytical methods must be used for a complete analysis.

ANALYSIS OF TEST BOARD B

A sample ($1 - 2\text{ mm}^2$) was taken from test board B including wood, primer and all the varnish layers. All raw materials mentioned in recipe B should have been present in this sample. The sample was taken through all the layers and analyzed as one, because the composition of each of the layers was identical, and also because the layers were so thin that even by the use of a micromanipulator they could not be separated.

Infrared spectroscopy

Since the substances present in the sample must be dissolved for the analysis various solvents were tested for their suitability. These included the following: ethyl alcohol, diethyl ether and chloroform. There were no apparent differences between the spectra of the residues from the various solvents. Chloroform was thus

chosen for further procedures because not only oils and resins, but also waxes which may be present can be dissolved in it. The sample was treated as follows: A few ml of chloroform were added to the sample. This mixture remained approximately 12 hours at room temperature (ca 20 - 22°C). It was then heated a few minutes at 50°C. The chloroform was evaporated. The residue was mixed with potassium bromide (KBr) and pressed into a micropellet 1.5 mm in diam. The infrared spectrum of this pellet was then recorded.

Results

The spectrum indicated that a resin and an oil were present in the sample. Since the various specific peaks overlapped each other, it was not possible to determine precisely which oil and resin were present.

Infrared spectroscopy can be used to indicate the presence of an oil, resin, or wax. In most cases, however, it is not possible to determine which type of oil, resin, or wax.

The ethereal oils are an exception. These do not form a peak at 720 cm^{-1} , the specific peak for oils and therefore cannot be identified at all by means of IR when in a mixture.

Thin layer chromatography

The sample was heated several minutes with chloroform, to boiling point (61°C). The extract was used for the chromatographic analysis.

The KBr pellet, which already been used for the IR analysis, was crushed again and extracted with cold chloroform. After several experiments, it appeared that the chloroform extract from the KBr pellet resulted in a superior separation of components.

Another advantage of using the KBr pellet is that only one sample is required for both IR and TLC.

As a result the above mentioned method was used. The extract was then applied to the TLC-plate using a Pasteur pipette which had been drawn to a fine capillary (0.1 mm in diam.).

The thin layer plate was eluted three times with a chosen solvent, allowing it to dry between elutions. Carrying out the elution three times gives a superior separation of components. Once dry, the chromatogram was sprayed with the detection reagent and assessed under ultraviolet light at 366 nm.

Results

From the chromatogram, it was possible to identify colophony. Although crude linseed oil and alizarin could be identified as raw materials using the system for resins, they could no longer be identified in the analysis of test board B's mixture. This was presumably due to the low concentrations of these substances, such that they remained below detection limit in the system. Moreover, the R_f values of their main components coincide.

A second sample was tested for the presence of steroids to indicate oils, and by the system for red natural dyes to indicate alizarin.

The distinction between gum turpentine and colophony was also no longer possible with the sample from test board B. Both colophony and turpentine oil are present in gum turpentine. After the gum turpentine dried, those components which could have been identified in fresh gum turpentine using TLC, have disappeared. The only substance which could still be identified using TLC was colophony.

Conclusion test board B

By microscopic analyses such as those mentioned previously, it is not possible to determine exactly how many varnish layers have been applied, but it is possible to see between which layers the varnish has been ground.

When analyzing samples, infrared spectroscopy can indicate the presence of an oil, resin and/or wax. Ethereal oils cannot be detected. If sufficient sample material is available, then the oil can be identified. This is also possible using the TLC test for steroids.

Colophony can be identified using the TLC separation system for resins. No distinction is possible between gum turpentine and colophony.

Alizarin can be identified using the TLC system for red dyes. In order to identify oils, resins and also dyes in the varnish, it is necessary to take either a relatively large sample, or three smaller samples so that the various analytical methods can be applied.

Analysis of test boards A through J

Taking into account the results obtained with board B, the other nine test board samples were also examined.

Microscopic work was not carried out, because previous results on board B did not justify it. The following procedure was chosen for the analysis.

A sample was taken from the last section of each board. This section included all layers which had been applied. The entire sample was kept under chloroform in a closed test tube for about 12 hours at room temperature. The sample was then heated with the chloroform several minutes at about 50°C.

The chloroform was evaporated from the extract, and the residue mixed with KBr and pressed into a micropellet for an infrared spectrum.

The pellet was then finely ground in a mortar, and extracted with chloroform at ca. 20°C. The resultant extract was used for the following thin layer chromatographic analyses:

- steroid test for the identification of oils
- analysis of resins
- analysis of dyestuffs.

All these analyses could only be carried out because the sample was relatively large (1 - 2 mm²).

Results of the test boards

If the infrared spectra only indicated the general presence of an oil, resin, or wax, but not the specific type of each respective substance, the result was recorded as, e.g. "oil +". The name of a specifically identified substance was indicated as, e.g. "linseed oil +". Where no identification was possible the marking " - " was used. The method of separation which was used was not recorded.

Test board A: Fulton-Thompson (12, 52, 53)

Ingredients	Results	
	IR	TLC
polymerized gum turpentine		-
piccolyte		-
crude linseed oil	oil +	linseed oil +
non-polymerized gum turpentine	resin +	gum turpentine +
alizarin		-
iron oxide		-

Remarks:

In test board A, it was possible to identify positively linseed oil and gum turpentine. The difference between polymerized and non-polymerized gum turpentine was not evident. Alizarin could not be detected, probably due to the low concentration. Piccolyte is a contemporary terpene and cannot be analyzed by the TLC separation system for resins. The presence of iron oxide was not analyzed. It could have been done by x-ray diffraction, Laser microspectral analysis, or microchemical analysis, but would have required a new sample.

Test board B: Pisters

Ingredients	Results	
	IR	TLC
gum turpentine		gum turpentine or
heated colophony	colophony +	colophony +
linseed oil	oil +	linseed oil +
alizarin		-

Remarks: see conclusion test board B (grid number 5)

Test board C: Mailand oil varnish (33)

Ingredients	Results	
	IR	TLC
gummigutti		gummigutti +
aloe		
polymerized gum turpentine		-
mastic	resin +	mastic +
dammar		-
crude linseed oil	linseed oil+	linseed oil+

Remarks:

In test board C it was possible to identify linseed oil and mastic. Dammar and polymerized gum turpentine could not be identified, probably because of the low concentration. The separation of aloe and gummigutti was not distinct enough to allow them to be identified in mixtures with the analytical methods used in this project.

Test board D: Mailand spirit varnish (33, p. 65)

Ingredients	Results	
	IR	TLC
sandarac	sandarac+	-
mastic		mastic +
elemi		elemi +
turpentine oil		
ricinus oil		

Remarks:

By combining both IR and TLC, three resins in this mixture could be identified, viz. sandarac, mastic and elemi.

Test board E: Propolis varnish Sacconi (48)

Ingredients	Results	
	IR	TLC
propolis	propolis+	propolis +
mastic	resin	mastic +
sandarac		-
dammar		-
eucalyptus oil		oil +
spike oil		
alizarine		alizarin+(weak)

Remarks:

In this mixture, only mastic and propolis could be positively identified. The identification of alizarin was only very slightly positive and probably only identified at all because of foreknowledge. Using the steroid test it was possible to distinguish between linseed oil and an ethereal oil. No distinction could be made between eucalyptus oil and spike oil with these two methods.

Test board F: Pisters

Ingredients	Results	
	IR	TLC
sandarac	resin +	-
linseed oil	linseed oil+	linseed oil +

Remarks:

Only linseed oil was positively identified. The resin concentration was probably too low for identification of type.

Test board G: Pisters

Ingredients	Results	
	IR	TLC
mastic	resin +	mastic +
colophony		-
linseed oil	linseed oil+	linseed oil +
gum turpentine		-
hartshorn salt		

Remarks:

Linseed oil and mastic were positively identified. The concentration of the other resins was probably too low. Hartshorn salt is a combination of ammonium bicarbonate NH_4HCO_3 and ammonium carbamate $\text{NH}_4\text{CO}_2\text{NH}_2$, and cannot be identified with the analytical methods used here.

Test board H: Pisters

Ingredients	Results	
	IR	TLC
mastic	resin +	mastic +
linseed oil	linseed oil+	linseed oil+
hartshorn salt		

Remarks:

With a simple recipe like this and sufficient concentrations, the presence of linseed oil and mastic were clearly indicated.

Test board I: Michelman no 1 (36)

Ingredients	Results	
	IR	TLC
colophony	resin +	colophony or gum terp. +
gum turpentine		
linseed oil	oil +	linseed oil+
alizarin		alizarin +
iron oxide		
dragon's blood		dragon's bl+

Remarks:

As previously mentioned, it is not possible to distinguish between gum turpentine and colophony. However, the main component common to both was positively identified.

Alizarin and dragon's blood were also positively identified. Linseed oil was positively identified by the steroid test.

Test board J: Simon no 3

Ingredients	Results	
	IR	TLC
shellac	resin +	shellac +
sandarac		sandarac +
copaiba balsam		-
Venice turpentine		-
linseed oil	linseed oil+	linseed oil+
dragon's blood		dragon's bl+
gummigutti		-

Remarks:

From this analysis it seems that if the concentrations are high enough, a mixture of three resins can be analysed. In this case, shellac, sandarac and dragon's blood were identified. Linseed oil was also positively identified. The mixture was, however, complex and some of the concentrations were small. Copaiba balsam and Venice turpentine could not be identified.

Final conclusion:

From the test board results, it appears that a complete identification of all the ingredients of a mixture of a violin varnish is very difficult, if not impossible. In our case the results could have been positively affected by foreknowledge of the materials which have been used. The results from the various test boards were very inconsistent.

Sometimes, three resins could be positively identified from a mixture, while other cases only one, or even only the general class: "resin +" could be identified.

This was closely connected with the concentration of the different resins, both in absolute terms and relative to each other. The size of the sample also played an important part.

In spite of the minimal sample size, the analysis of a sample containing mixtures of several resins and an oil still produced good results. In other words, the main components in each recipe could be definitely identified.

However, in order to carry out as thorough an analysis of the mixture, as possible, at least three analytical methods must be used; viz. infrared spectroscopy, TLC for resins, TLC for dyes and the TLC steroid test or gas chromatography for oils.

This means that either several samples must be taken, or one relatively large one (approx. 3 mm²).

Even with a large sample, though, the analysis of resin mixtures remains complex. Some mixtures can be analyzed, for example those containing either shellac and sandarac or mastic and elemi. In mixtures containing colophony or gum turpentine no distinction can be made between these two substances. With mixtures on old instruments, the analysis will be even more difficult as the chemical composition of the varnish will have changed through ageing and the compounds will have become less soluble.

BIBLIOGRAPHY

1. Van Asperen de Boer, J.R.J., Some Practical Aspects of the Preparation and Study of Cross-sections. ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen, 1984.
2. Bachmann, A., Encyclopedia of the Violin, Editor A.E. Wier.
3. Bletschacher, R., Die Lauten und Geigenmacher des Fussener Landes, Hofheim, 1978.
4. Bull, R., Das grosse Buch vom Wachs, Geschichte, Kultur, Technik, I, II, Muchen, 1977.
5. Castle, F., Violintone peculiars, Editor C. Farseth, Minneapolis, 1906.
6. Condux, L., Final Summary Report of Violin Varnish Research Project, Mellon Institute Report no. 3070, Pittsburg, 1970.
7. Feller, R., Dammar and Mastic infrared Analysis, Science, 1954, Vol. 120.
8. Flett, M.St.C., Characteristic Frequencies of Chemical Groups in the Infrared, Amsterdam 1963.
9. Frei, M., Naturwissenschaftliche Methoden zur Aufdeckung von Geigenfälschungen, Archiv Kriminol. 116 (1955) 125-138.
10. Fry, G., The Varnishes of the Italian Violinmakers etc. London, 1904.
11. Fuhr, K., Das Akustische Ratsel der Geige, Frankfurt, 1958.
12. Fulton, W.M., Old Italian Varnish, The Strad, 1974, 491-501.
13. Ghisalberti, E.L., Propolis, A Review. Bee World, 60(2), 1979, 59-84.
14. Greilsamer, L., L'Anatomie et la Physiologie du violon d'alto du violoncelle suivies du vernis de Cremona, Paris, 1924.
15. Hallebeek, P., Microscopisch en Microchemisch Onderzoek van Kunstvoorwerpen. Conserveren-Restauration, 1972, 2, p. 3-10.
16. Heinen, W., Linskens, H.F., On the occurrence of fatty acids in propolis, University of Nijmegen, 1971.
17. Heron-Allen, Ed., Violinmaking as it was and is. London 1885.
18. Hill, W.H., A.F., A.E., Antonio Stradivari, his life and work, New York, 1963.
19. Hill, A., A. & W.H., The violin makers of the Guarneri Family, London, 1965.
20. Hofenk de Graaff, J.H., Roelofs, W.G.Th., On the occurrence of red dyestuffs in textile materials from the period 1450-1600, ICOM Madrid, 1972.
21. Hofenk de Graaff, J.H., Roelofs, W.G.Th., The analysis of flavonoids in natural yellow dyestuffs occurring in ancient textiles, ICOM 5th Triennial Meeting, Zagreb, 1978.
22. Howes, F.N., Vegetable Gums and Resins, Waltham, 1949.
23. Van 't Hul, E.H., Infrared microspectroscopy for the analysis of old painting materials, Studies in Conservation, 15(1970), 3, p. 175-182.
24. Hummel/Scholl, Hochpolymere und Harze. Atlas der Kunststoff-Analyse, Band 1, Teil I, Munchen, 1968.
25. Hummel/Scholl, Hochpolymere und Harze. Atlas der Kunststoff-Analyse, Band 1, Teil II, Munchen, 1968.
26. Hurst, G., Painters, Colours, Oils and Varnishes, London, 1896.
27. Jalovec, K., Beautiful Italian Violins, London, 1963.
28. Knopf, E., Der Cremoneser Lack, Eine Studie über Geigenlackuntersuchungen, Frankfurt, 1979.
29. Kolattukudy, P.E., Chemistry and Biochemistry of Natural Waxes, Amsterdam, 1976.
30. Kühn, H., Detection and Identification of Waxes, Including Punic Wax by Infra-red. Studies in Conservation 5, 71, 1960.
31. Leipp, E., The Violin, Toronto, 1969.
32. Van der Maas, J.H., Basic Infrared Spectroscopy, Bath, 1972².
33. Mailand, E., Das wiederentdeckte Geheimnis des Altitalienischen Geigenlackes, Leipzig, 1903.
34. Masschelein-Kleiner, L., Taets, P., Contribution to the Study of Natural Resins in the Art. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981.
35. Matteini, M., Moles, A., Tosini, I., Topochemical Reactions for the Recognition of Oil Media in paint Fragments. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981.
36. Michelman, J., Violin Varnish, Cincinnati, 1946, Appendix, 1958.
37. Millant, R. & M., Manual Practique de Lutherie, Paris, 1952.
38. Millant, R., Vuillaume, J.B., Sa vie et son oeuvre, London, 1952.
39. Mills, J.S., The Gas-Chromatographic Examination of Paint Media part I, Fatty Acids Composition and Identification of Dried Oil Films, Studies in Conservation (1966) 92-107.
40. Mills, J.S., White, R., The Gas-Chromatographic Examination of Paint Media Part II, Conservation and Restoration of Pictorial Art, London, 1976, 72-77.

41. Mills, J.S., White, R., Natural Resins of Art and Archeology. Their Sources, Chemistry and Identification. Studies in Conservation, 22 (1977) 12-31.
42. Mockel, O., Winckel, F., Die Kunst des Geigenbaues, Berlin-Steglitz, 1930.
43. Niederheitmann, F., Altmann, W., Cremona, Leipzig, 1928. 7.
44. Peterlongo, P., Die Streichinstrumente, Frankfurt, 1976.
45. Randerrath, W., Dünnschicht Chromatographie, Weinheim, 1965.
46. Rodig, J., Geigenbau in Neuer Sicht, Frankfurt, 1976.
47. Roelofs, W.G.Th., Thin layer chromatography: An aid for the analysis of binding materials and natural dyestuffs from works of art. ICOM Committee for Conservation, Madrid, 1972.
48. Sacconi, S.F., Die Geheimnisse Stradivaris, Frankfurt, 1972.
49. Sander mann, W., Naturharze, Terpentinöl, Tallöl, Berlin, 1960.
50. Schramm, H.P., Hering, B., Historische Malmaterialien und Möglichkeiten ihrer Identifizierung, Dresden, 1980.
51. Stahl, E., Thin-layer Chromatography, New York, 1965.
52. Thompson, R.P., A Modification of Fulton's Old Italian Varnish Catgut Acoustical Society, Newsletter no. 29, pp. 35-36.
53. Thompson, R.P., Coloured Terpene Resin Violin Varnish - A new Approach.
55. Wake, S., Technique of Violinmaking, San Diego, 1973.
56. Walker, A.P., IBRA Bibliography no. 16. Annotated Bibliography on propolis, 1976. International Bee Research Association, Bucks, England.
57. Weber, V., Das Wachsbuch, Munchen, 1975.
58. White, R., An Examination of Varnish from three eighteenth century musical instruments. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978.
59. White, R., A review with illustrations to the analysis of resin/oil varnish mixtures. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, 1981.
60. White, R., The application of gaschromatography to the identification of waxes. Studies in Conservation 23 (1978) 57-68.



SUMMARY

THE RELEVANCE OF PREFERENTIAL SURFACE YELLOWING IN THE LIGHT-AGING OF POLYMERS FOR CONSERVATION

Norman H Tennent and Joyce H Townsend
Glasgow Museums and Art Galleries
Kelvingrove
Glasgow G3 8AG
Scotland

Introduction

The prediction of polymer durability has become increasingly important in recent years. As the range of commercially available polymers increases, so does the need to develop valid methods of evaluation, prior to their use in conservation. Fortunately, not only has the number of laboratories involved in assessing polymer stability for conservation increased but, concurrently, the testing procedures have become more sophisticated (see, for example (1)). Nonetheless, the assessment of polymer stability is a very complex area of conservation research and many factors need to be taken into consideration, especially when accelerated aging tests are performed (1).

In general terms, the conclusions drawn from accelerated aging tests depend on the polymer property which is being monitored and the conditions under which the test programme is executed. In the accelerated light aging of polymers, degradation may take the form of chalking, yellowing, embrittlement, loss of adhesion, etc and the results of evaluation of any one of these properties will be dependent on factors such as the spectral distribution of the light source, the temperature of the sample and the relative humidity in the sample cell. Even with a clear appreciation of the issues involved in the prediction of polymer stability from accelerated aging tests it is difficult to ensure that full account is taken of all the relevant factors.

One such factor was discussed by Thomson over 20 years ago (2) but has subsequently received little attention. When a clear resin yellows as a result of light exposure, preferential yellowing at the surface nearer the light source often occurs. The reason for this is, primarily, that once the polymer surface has become sufficiently yellow it acts as a filter which shields the remainder of the sample from degradation. Thomson described equations which could be used to calculate the amount of light passing through a thin film at a given depth from the surface, and the proportion of degraded or undegraded material at that depth. This was demonstrated graphically for a film, 0.01mm thick, which is initially transparent and then yellows on exposure to light of arbitrary intensity. As the upper surface of the film degrades and grows yellow, successively less light reaches the lower portions of the film. If the film yellows rapidly the stage is quickly reached where the remainder of the sample is completely shielded from further damage. If the film yellows slowly, ultraviolet light passes through the whole sample which is, in its entirety, susceptible to damage.

This phenomenon has considerable implications in the testing of resins for any conservation process which involves the use of resins in appreciable thickness, for example the use of clear polymers for adhesives or gap fillers in glass conservation. The purpose of this paper is to present preliminary experimental evidence on the preferential surface yellowing of certain epoxy resins and to indicate some uncertainties in the prediction of long-term yellowing of thick casts on the basis of results with thin films.

ExperimentalResin Samples

The commercially-available resins, Araldite AY103/HY951 and Devcon 2-Ton, both amine-cured, diglycidyl ether Bisphenol-A type epoxy resins, were weighed and mixed in the appropriate proportions and were cured at room temperature. The UV-curing epoxy, designated Uvepox in this paper, is a laboratory formulation, not available commercially, based on the diglycidyl ether of Bisphenol-A.

The casts were made on Melinex polyester film with spacers made from one to three microscope slides for the thicker ones, or were pressed between two sheets of Melinex in the case of the thin films. The most uniform portions were cut out. The average thickness of each cast was obtained from micrometer measurements at six different points on the surface of the final cast. The

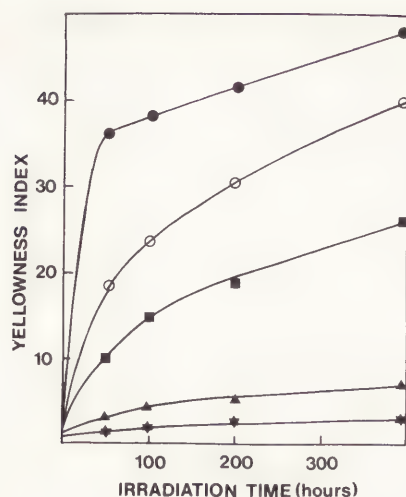


Fig 1: The yellowness index of Uvepox resin during aging. (●) thick cast, 1.52mm thick, (○) sandwich of 5 layers, 1.11mm thick in total, (■) top layer of the sandwich, 0.26mm thick, (▲) second layer of the sandwich, 0.22mm, (★) remaining layers (all 3 had the same YI at each stage).

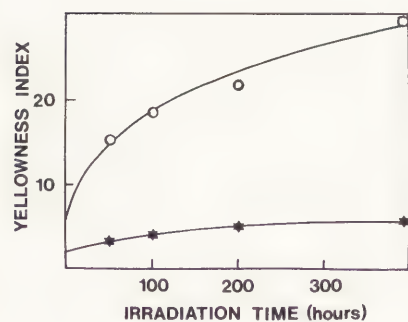


Fig 2: The yellowness index of Devcon 2-Ton epoxy during aging. (○) sandwich of 5 layers, 0.93mm thick in total, (★) individual layers of the sandwich (all 5 had the same YI at each stage)

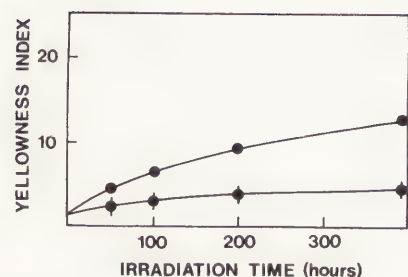


Fig 3: The yellowness index of thick casts (1.12mm) of Araldite AY103/HY951. (●) no filter, ie normal type of exposure, (◆) filtered with a thick (c.1mm), well-yellowed cast of AY103/HY951.

thick casts (1-3mm) varied in thickness by c.5% over each cast, while the thin ones showed more variation. Sandwiches consisted of 5 layers in a definite sequence, and each 0.2-0.4mm thick, depending on the resin. The variation in thickness among the layers was $\pm 20\%$, though sometimes layer 5 (the lowest) was by far the thickest.

Accelerated ageing

The casts were placed inside the glass sample cells of a Microscal Lightfastness Tester, which has been described elsewhere (3). A 500W MBTL (high-pressure mercury tungsten) bulb was used to irradiate them for up to 1000 hours. The air temperature in the cell was maintained at c.30°C air temperature/55°C black panel temperature by means of a cooling fan.

Yellowness index measurements

Tristimulus values X, Y, Z (in terms of the C.I.E. 1931 standard observer) were calculated from the transmittance spectrum of each sample, relative to a standard white plate (barium sulphate)*. Yellowness indices were calculated at each stage of aging from these results. Yellowness Index (YI) is defined in terms of X, Y, Z for the C.I.E. light source C (which represents daylight at 6500K, rather deficient in ultraviolet light; a suitable approximation to museum lighting):

$$YI = 100(1.28X - 1.06Z)/Y$$

The change in yellowness index, ΔYI is

$$\Delta YI = YI(\text{after aging}) - YI(\text{before aging})$$

This is meant to express the increasing yellowness of a clear resin on a simple, numerical scale, which relates to increasing yellowness as perceived by the eye. (If a sample were on the blue side of yellow, then YI would be negative, or if it were bleached and became more transparent on aging then ΔYI would be negative). In effect, it is a colour difference in one dimension (yellow/blue). The experimental error (due principally to imperfections of the sample surface) is about twice that for a CIELAB colour difference (4), ie ± 1.5 units of YI.

Results and Discussion

Of the three epoxy formulations examined in this investigation, Uvepox exhibits the most rapid yellowing and shows the most pronounced surface yellowing effect (Figure 1). Although this resin is initially clear and colourless, rapid yellowing of a thick, >1mm cast occurs (● in Figure 1). Rapid yellowing also occurs in the sandwich of 5 layers (○ in Figure 1) but the great preponderance of this yellowing is restricted to the upper layer of the sandwich (■ in Figure 1). From the outset the marked yellowing of the upper layer shields the remaining layers so that the rate of yellowing of layer 2 is only moderate while the remaining layers show, relatively, minimal yellowing.

In contrast, for both the Araldite AY103/HY951 and Devcon 2-Ton samples, although yellowing is fairly pronounced, the plots of yellowness index after 400 hours aging show no differential in the yellowness of the layers which comprise the sandwich. This is illustrated for Devcon 2-Ton in Figure 2. The overall yellowness of the sandwich is the result of the combined yellowness of the individual layers, each of which behaves similarly. The plots for Araldite AY103/HY951 are similar to Devcon 2-Ton and are not reproduced here.

The reason for the lack of evidence of shielding in the plots of these resins is that the degree of yellowing is not pronounced enough to cause the surface of the resin to protect the bulk of the resin sample. That this does become important is illustrated by Figure 3, the increase in yellowness index of casts (c.1mm thick) of Araldite AY103/HY951 during light aging. If from the outset the sample is protected by a yellow filter (consisting of a 1mm AY103/HY951 cast after 1000 hours of MBTL light aging), then the rate of yellowing is reduced significantly (◆ in Figure 3) compared to the unprotected resin (● in Figure 3).

In a separate experiment, a thick cast of Aradite AY103/HY951 was examined after 1000 hours of MBTL light aging had resulted in significant yellowing. By progressively grinding away the top surface and recalculating the yellowness index of the remaining sample it was established that the yellowness was most pronounced

* In a previous paper by the present authors (4) it was stated, incorrectly, that reference samples were of standard magnesium oxide

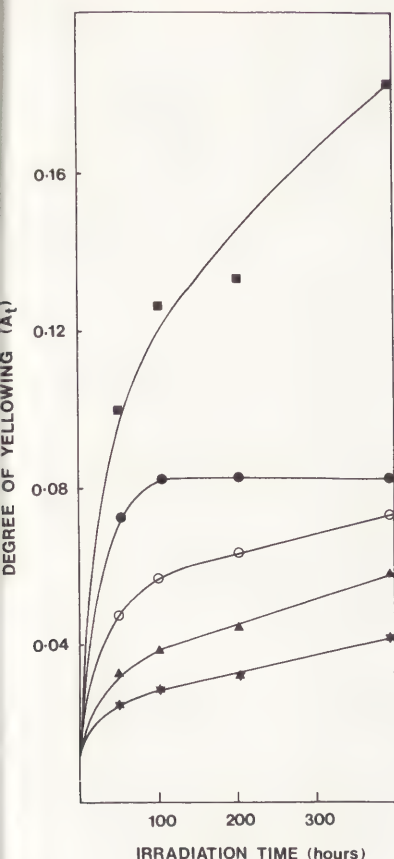


Fig 4: The degree of yellowing of Uvepox resin as a result of aging. (●) thick cast, 1.52mm thick, (○) sandwich of 5 layers, 1.11mm thick in total, (■) top layer of the sandwich, 0.26mm thick, (▲) second layer, 0.22mm thick, (★) third layer, 0.20mm thick

in the top 0.2mm, the remainder being fairly uniform in colour.

Yellowness index is but one possible way of expressing the extent of yellowing of a resin sample. In an exceptionally thorough investigation of the light aging of epoxy resins, Down adopted an expression for the degree of yellowing, A_t , defined as follows (5):

$$A_t = (A(380\text{nm})_t - A(600\text{nm})_t) \times 0.1\text{mm}/F$$

where A_t = degree of yellowing

A = absorbance

t = time

F = average film thickness for each sample

The validity of this expression depends on the samples' showing no surface yellowing effect, ie they should display uniform yellowing throughout their whole thickness (F) at all stages in yellowing.

When the results in Figure 1 for the yellowing of Uvepox are replotted in terms of the degree of yellowing, A_t , defined above, the resultant plots show a considerable differential in behaviour (Figure 4). Ideally, if there were no preponderance of surface yellowing, the separate plots in Figure 4 would be coincident. The widely differing behaviour exemplified by the plots of Figure 4 indicate that A_t can be misleading if the sample is thick enough to allow surface yellowing to come into play.

Unfortunately there is very little information on what is likely to be the limiting sample thickness which will ensure uniform yellowing throughout the sample. In an investigation of the degradation of picture varnishes, c.0.01mm thick, uniform yellowing occurred (6). In other studies it has been observed that the degradation of polycarbonate sheets exposed to natural weathering is limited to a depth of 0.1mm from the surface (7,p159-161) while the photo-oxidation of low-density polyethylene predominates in the outer 0.5mm (7,p118-119).

The results for the more extended light aging of Araldite AY103/HY951 shown in Figure 5 indicate a differential in behaviour of the degree of yellowing plot for a 0.08mm film compared to a 0.38mm film. Thus, even for relatively thin films discrepancies can occur due to non-uniform yellowing.

The thickness of film which displays uniform yellowing is likely to depend on the polymer under investigation. For appreciably thick films, restricted oxygen diffusion into the polymer is likely to depend on factors such as the crystallinity and cross-link density of the resin. It has even been proposed that degradation can be inhibited by modifying the physical or chemical surface of a polymer (8,p191-192). The extent of the shielding effect of a yellow surface will also be polymer-dependent, relating as it does to the sensitivity of the polymer

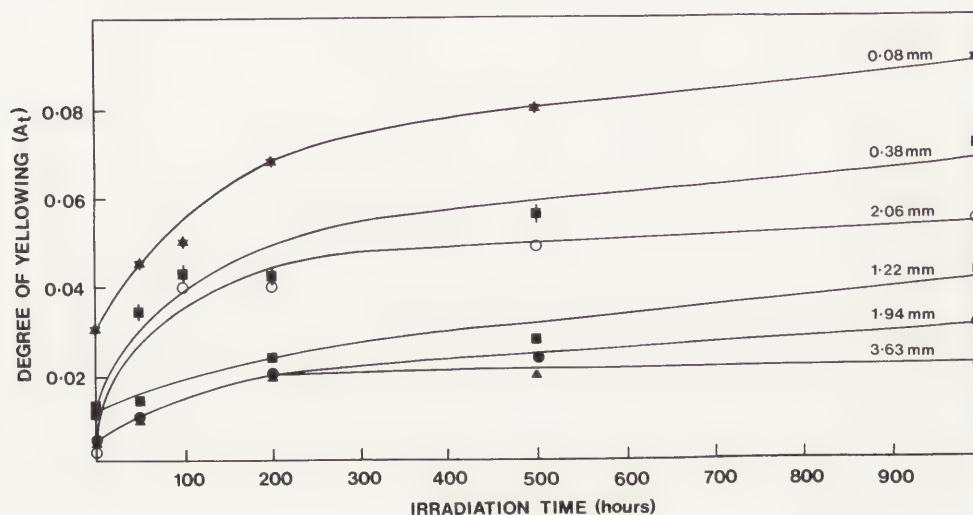


Fig 5: The degree of yellowing of Araldite AY103/HY951 as a result of prolonged aging. (○) represents a sandwich, otherwise casts were solid, of the indicated thickness

to degradation by specific wavelengths of light.

There is some evidence of the role of oxygen diffusion in the plots of Araldite AY103/HY951. Although no shielding effect is evident at early stages in the resin yellowing, the degree of yellowing plots (Figure 5) indicate predominant surface yellowing, quite possibly the result of limited oxygen diffusion into these samples.

Conclusions

The results from the light-induced yellowing of the three epoxy resins discussed in this preliminary paper indicate that surface yellowing can be a significant factor in assessing the degradation of films greater in thickness than c.0.1mm. Factors such as oxygen diffusion and the filter effect of a yellow surface layer can result in non-uniform yellowing throughout the sample thickness. This has implications for the prediction of the degree of yellowing of thick films based on the results with thin films, and care must be taken to avoid overestimation of the yellowing of thicker films.

The results also have bearing on measures which might be taken to limit the yellowing of unstable resins. These factors are under investigation and will be reported in due course.

References

1. R.L. Feller, "Some Factors to be Considered in Accelerated-Aging Tests", AIC 15th Annual Meeting (1987), in the press
2. G. Thomson, "Topics in the conservation chemistry of surfaces", in Application of science in examination of works of art, Museum of Fine Arts, Boston (1965)
3. G.H. Giles, C.D. Shah, and D. Baillie, "Economical and Efficient Fading Lamps", J. Soc. Dyers and Colourists, 85 (1969): pp.410-417
4. N.H. Tennent and J.H. Townsend, "The photofading of dyestuffs in epoxy, polyester and acrylic resins", ICOM Committee for Conservation 7th Triennial Meeting, Copenhagen (1984): 84.16.8-84.16.11
5. J.L. Down, "The yellowing of epoxy resin adhesives: report on high-intensity light ageing", Studies in Conservation 31 (1986): pp159-170.
6. René de la Rie, personal communication
7. A. Davis and D. Sims, Weathering of Polymers, Applied Science Publishers, London, 1983
8. W.L. Hawkins (ed.), Polymer Stabilization, Wiley-Interscience, New-York, 1971

SUMMARY

A method has been developed for the adhesion of flaking paint on ethnographic artefacts using water-based adhesives. These have a distinct advantage over solvent-based resins in that they cause much less darkening of paint, particularly when used with matt, porous paint typical of Oceanic painted artefacts. Since the formulation of many water-based resins, particularly emulsions and dispersions, is more complex and potentially less stable than pure resins, thorough testing is needed before resins can be selected and used with confidence. Testing and evaluation procedures have been designed to predict the performance, appearance and ageing characteristics of resins being considered for the adhesion of flaking paint. Both quantitative and subjective evaluation procedures are used. Where possible, resins are evaluated in combination with painted wood facsimiles of artefacts, rather than in isolation, to enable the assessment to be made under conditions that relate more directly to the way resins are actually used in conservation. Resin application, sample preparation and accelerated ageing techniques are described, as well as progress on tests to be used to assess appearance, pH, flexibility, adhesion, stability and the effect of temperature on the performance of resins.

INVESTIGATION INTO METHODS AND MATERIALS FOR THE ADHESION OF FLAKING PAINT ON ETHNOGRAPHIC OBJECTS: A PROGRESS REPORT

S. Walston, D. Horton-James and S. Zounis

Australian Museum
6-8 College Street
SYDNEY N.S.W. 2000

INTRODUCTION

Conservators of ethnographic painted objects have been grappling with the problem of consolidating loose paint surfaces for a long time, but unqualified successes have rarely been recorded. The most common complaints are that resins tend to change the appearance of objects, particularly those with porous paint layers, or that their ageing characteristics are not well enough known to enable many of them to be used with confidence.

Down¹, in describing the planning stages of the CCI resins testing programme, reports that "...most adhesive concerns revolved around one theme: there was little information concerning the change in behavior of adhesives with time."

Our motivation for entering into the resins research field is simply that we are totally unable to conserve a large proportion of painted artefacts in the Australian Museum: the commonly accepted methods and materials used for the adhesion and consolidation of painted surfaces do not work well enough for Oceanic artefacts.

While there is no shortage of resins on the market, the problem is sorting out which ones will work for a particular conservation problem; in our case, the adhesion of flaking paint.

The purpose of the project is therefore, in addition to developing a suitable flake adhesion techniques, to establish a series of evaluation procedures for identifying which of the commercially available resins will perform best for this specific consolidation application. In practical terms, we want to be able to select resins that have the following properties:

- a) suitable working properties for the particular application techniques to be used;
- b) physical and chemical compatibility with the paint layer and support;
- c) suit the environmental conditions for which they are to be used;
- d) cause minimum change to the appearance of the object;
- e) form a sufficiently flexible bond between the paint and support to ensure good adhesion between materials with different levels of expansion and contraction;
- f) maintain long term stability.

A further requirement is that all test procedures should be able to be carried out by conservation staff on a routine basis. Also that costs should be kept as low as possible, preferably within the normal operating budget of an average museum conservation laboratory.

Artefacts from the Australian and Pacific region, with which we are chiefly concerned, are typically painted with clay and ochre pigments that contain little or no binding media. They tend to be extremely porous, have a matt surface and are very subject to crumbling or flaking. Consolidation with solvent-based resins almost always results in an unacceptable level of colour change, irrespective of the solvents used or

the concentration or method of application.

Welsh² reported successful results using Acryloid B72 in diethylbenzene for the consolidation of loosely bound pigments on palm spathe, and I'ons³ reported similar findings using acetoacetate. We have not, however, found that these solvent systems achieve sufficiently good results to warrant pursuing this approach, although the use of slow evaporation solvents does provide some improvement to the performance and appearance of solvent-based resins.

Pilot studies carried out by Walston and Gatenby^{4&6} and Gatenby and Gaulton⁵ however, indicated that a range of water-based resins within the PVA emulsion, acrylic dispersion and cellulose ether groups had potential for the consolidation of painted ethnographic objects. The working properties, performance and appearance of many of these resins appeared to work well for both surface consolidation and flake adhesion application and deserve further investigation.

We decided, therefore, to concentrate on water-based resins and initially focus our investigation on finding methods and materials that could be used for the adhesion of flaking paint, rather than tackle the whole spectrum of paint consolidation as a single project.

The investigation has been designed in three stages. The first is to develop resin application techniques, the second to develop resin selection and evaluation procedures, and the third to test the performance, appearance and stability of selected resins.

This work is not yet completed so this paper is presented as a progress report: there are still some tests to be finalized for Stage II, and Stage III has not been started. It is important to emphasize that, as the first two stages are concerned primarily with establishing techniques rather than with evaluating specific resins, this paper does not discuss the qualities of specific resins. That will be addressed in Stage III of the project.

1. STAGE I: FLAKE ADHESION TECHNIQUE

1.1 Aims

The object of the technique is to introduce beneath the flake the minimum quantity of resin necessary to ensure a good bond with the support, requiring little or no clean up.

1.2 Method

A spatula for applying the resin is made from a strip of 0.09mm thick polyethylene film approximately 30mm long which is cut to the width of the flake and mounted in locking forceps. Normally a stock selection is prepared in advance. The quantity of resin needed to thinly coat the cleavage area is painted onto the upper surface of the polyethylene strip. This is quickly introduced beneath the flake and the strip withdrawn as the resin transfers to the paint and support materials. Speed is essential otherwise the resin becomes tacky and pulls the paint away when the polyethylene strip is withdrawn. A slightly moistened tissue-covered cotton wool pad is gently pressed over the flake to position it. The moisture on the surface of the pad acts both as a temporary release agent and, together with the moisture from the emulsion or dispersion, relaxes the paint flake so that it can be safely repositioned. The pad also absorbs excess resin but only if it is applied before the resin becomes tacky or any skinning occurs. A dry pad is finally pressed gently over the flake area to absorb any excess moisture. A dry pad can be used for the whole operation if the flake requires only minimal repositioning and the correct quantity of resin is used. Resin that penetrates through to the surface of the paint or squeezes out around the edges of the flake when it is laid down tends to cause discolouration or gloss and it is seldom possible to remove excess resin from such porous, fragile paint after it has set.

The success of this technique is dependent both on the skill of the operator and on the working properties of the resin, but when used skillfully, yields excellent results.

2. STAGE II: CHARACTERIZATION OF RESINS

2.1 Introduction

The aim of this part of the project is to establish evaluation procedures that can be used to predict the performance of resins as adhesives for flaking paint. It is important that these enable both objective and subjective evaluation of the resin to be made, both in combination with the paint and support materials and in isolation. Where possible, tests have been based on international standards for resin testing or adapted from resin characterization and testing programmes undertaken by other researches in this field.

Subjective tests are largely carried out on facsimiles designed to reproduce flaking surfaces on wooden objects, a condition common amongst ethnographic collections.

2.2 Preliminary selection of resins

The following criteria were adopted for the preliminary selection of resins for testing:

Liquid resin:

- water based
- good working properties
- non-toxic
- rapid setting at room temperature
- neutral pH
- colourless
- compatible with paint and support materials
- low shrinkage

Cured resin:

- flexible
- non-tacky
- colourless and transparent
- inert
- soluble in organic solvents
- good ageing characteristics

Manufacturers' technical data and the conservation literature were consulted and 23 resins that appeared to fit the criteria, and that were easily available in Australia, were obtained. Subjective evaluation of colour and flexibility of test castings eliminated all but 9 of these for use as working resins in the development of testing and evaluation procedures. Three additional resins were also included as standard references, as recommended by Feller.

A larger number of resins, particularly those that have been favourably reported on in the conservation literature or are currently under investigation (e.g. by Feller and at the Canadian Conservation Institute) will be used for Stage III of the project.

Before proceeding to the resin-testing programme, the 9 resins initially selected were tested for satisfactory working properties.

2.2.1. PRELIMINARY ASSESSMENT OF WORKING PROPERTIES, PERFORMANCE AND APPEARANCE

Aim: To ensure that resins selected for the main testing programme have suitable working properties, performance and appearance when applied to standard samples closely resembling objects with flaking paint.

Sample preparation: The materials used were yellow ochre (quartz/geothite) obtained from a traditional Aboriginal source, and a seasoned Australian hardwood (*Tristania conferta*) having similar properties to many of the painted wood carvings in the ethnographic collections.

The pigment was ground to the particle size typical of many Aboriginal pigments and mixed with a binding medium containing 3 parts gelatin, 1 part polyvinyl acetate emulsion wood adhesive and 96 parts water. Equal quantities of the paint slurry were applied by brush to seasoned wood samples

which were cut in the same plane from a single plank. The samples were then placed in an oven at 150°C to promote differential shrinkage between the timber and the paint layer. After two hours they were removed and allowed to cool at room temperature. The gelatin component was found to enhance the formation of both large and small paint flakes, similar to those occurring on Australian and Pacific artefacts. The PVA provided the degree of particle cohesion required, which could not be achieved by using gelatin alone.

The difficulty of obtaining sufficient quantities of traditional binding media (fresh orchid juice, spinifex resin, etc) and reproducing one of the many methods used for applying it to the support, or mixing it with pigment, precluded their use for experimental purposes.

Method: Resins are applied to the experimental samples using the flake adhesion technique described in section 1.2 and an assessment made of their working properties. These include the ease with which the resin can be introduced, the flake repositioned and excess resin removed from the surface. The treated samples are allowed to cure for seven days at room temperature.

The painted samples are then re-examined for any changes in appearance, particularly colour and gloss. Adhesion of the paint to the wood support is assessed using a probe and stereoscopic microscope. Penetration of the resin up through the paint layer is also noted.

Flake adhesion and evaluation processes are carried out by a minimum of two conservators using the same series of resin and sample replicates and a simple grading system to enable direct comparison of the resins.

Any resins that are clearly unsuitable are eliminated from the testing programme at this stage.

2.3 Testing programme

2.3.1 AIM

To develop a series of tests that can be used to assess the properties and performance of resins both in isolation and in combination with paint and support materials.

2.3.2 RESIN IN ISOLATION

Tests for the resins alone are predominantly quantitative and are designed to provide information on colour, pH, flexibility, solubility, tackiness and the effects of temperature. They are also designed to give an indication of the chemical stability of test resins by comparing the degree of change that has occurred after ageing.

All tests are performed initially at 22°C and 55% RH on samples of cured resin before and after accelerated light-ageing. These conditions may be varied at a later stage in the testing programme.

Sample preparation: A drawdown method, based on ASTM D823-84 - Method C¹⁰ is used to cast 0.30mm thickness films of resin having a thickness variation of less than 5%. The method was varied in that the motor driven film applicator specified in the Standard was replaced by a manual technique. From the cast film, samples measuring 50mm x 27mm are prepared for determining colour, solubility and pH, and samples measuring 80mm x 13mm are prepared for assessing flexibility using tensile testing apparatus. All samples are tested before and after they have been artificially aged.

Note on accelerated light-ageing method used

The method used is based on AS 2001.4.21-1979¹¹ in which resin samples are attached to an aluminium cylinder and exposed to a centrally mounted light source (Philips ML500W mercury vapour, tungsten filament, internally phosphor-coated lamp). The samples are exposed until Blue Wool Standard (BS1006:1978) No. 6 is reached (in accordance with Feller's¹² recommendation), which occurs after approximately

180 hours.

The procedure specified in the Standard was slightly modified in that a fan is placed over the ageing drum to reduce the temperature as far as possible without acquiring more complex cooling systems. The temperature of the resin is measured using a thermocouple embedded in one of the samples. This value, together with the absolute moisture content of the air is then used to calculate the RH at the surface of the resin using a psychrometric chart. Phillips TL37 lamps were originally intended to be used, however the number of tubes needed to reach the energy level required for accelerated ageing would have been too difficult to construct.

The spectral distribution of the ML500W lamp compares favourably to the TL37, both having a continuous spectrum and comparable mercury radiation peaks. In fact the ML500W lamp compares better to the TL37 than to daylight. The phosphor coating converts the shorter and more destructive UV radiation into longer UV or visible radiation, although there is more UV than the TL37. Compared to the other accelerated light systems the ML500W lamp has a low U.V. content.

In the longer term we may adopt natural dark ageing methods, the advantages of which are described by Down¹³, particularly if an intensive investigation of the more promising resins is undertaken.

2.3.2.1 Colour test

Aim: To establish whether resins are colourless and whether any change is likely to occur on ageing which would give an indication of their stability.

Method: Colour measurements are taken using a Minolta Chromameter II - Reflectance and Y x y (CIE 1931) and L a b (CIE 1976) co-ordinates plus colour difference (ΔE) are recorded.

A visual assessment of the resin is also made by three conservators using a Phillips TL37 light source (standard Australian Museum laboratory and display lighting) against a neutral background. The advantages of using more controlled viewing conditions as specified in various international standards (e.g. AS 1580 Method 601.1-1975¹⁴, ASTM D1729-69 [reapproved 1974]¹⁵ and BS 3900: Part D1:1978¹⁶) are still under consideration. Anderson and Wright¹⁷ have developed a standard viewing cabinet which may be of use in conservation.

All colour measurements and observations are carried out before and after the resin samples are light aged.

2.3.2.2 pH tests

Aim: a) to determine whether the pH of resins, in both the liquid and the cured state, is suitable for the treatment of artefacts.

b) To determine the ageing characteristics of resins by using change in pH as an indicator of chemical stability and to assess whether any change in pH which could damage artefacts is likely to occur with age.

Method: Liquid resin

pH measurements are taken of the liquid resin as supplied by the manufacturer according to the method specified in AS 1321.7-1977¹⁸.

Cured resin

pH measurements are taken of the cured resin film according to the method specified in ASTM D1583-61 (reapproved 1981)¹⁹, in which shredded film is stirred continuously in distilled water and pH readings of the extract are taken after 72 hours.

All measurements are taken with a combined glass electrode and pH meter (Radiometer Copenhagen, type PHM 28d).

2.3.2.3 Solubility test

Aim: The primary aim is to evaluate the chemical stability of resins by comparing their solubility before and after ageing. The secondary aim is to identify resins with good solubility characteristics which will enable minor cleanup of an object's surface after flakes have been positioned. (Full reversibility of the process is not possible with the existing level of technology).

Method: The solubility of a resin is determined by testing its solubility in a series of solvents of increasing strength (decreasing fd value on the Teas Chart) as recommended by Feller and Bailie²⁰.

The solvent with the highest fd value in which each resin dissolved fully is then used to determine changes in the solubility of the resin after ageing.

For resins that are not fully soluble in any of the solvents in the series, acetone, the strongest solvent having the lowest fd value, is used.

2.3.2.4 Flexibility test

Aim: To identify resins that are flexible enough to maintain a reliable bond between typically brittle paint and dimensionally unstable support materials. A further aim of the test is to determine whether any changes to the tensile properties of the resin are likely to occur with age.

Method: A tensile testing machine (Jay Jay Type T5000) is used to obtain the stress-strain curve of the resin as specified in ASTM D2370-82²¹, and a comparison of the stress is made at 10% elongation. This elongation factor was selected to allow for a wide safety margin, as even under extreme RH conditions, the dimensional changes in wood or other plant materials are below this level. (Resins with a yield point below 10% elongation are rejected). Measurements are repeated for aged samples to see whether any changes to their properties are likely to occur with time. The best indication of change can be obtained by comparing the elongation at break figures calculated from the stress-strain curve.

2.3.2.5 Tack test

Aim: To identify resins that do not have a tendency to trap dust under ambient temperature conditions. (This is significant where a resin penetrates through to the surface of the paint or cannot be fully cleaned from around the flake after application.)

Method: Test samples are exposed to a dusty environment for a fixed period. Loose dirt is then removed using either vacuum or positive air pressure to simulate laboratory cleaning techniques. The results are assessed subjectively using a stereoscopic microscope. The design for this test has not yet been finalized.

2.3.2.6 Cold flow test

Aim: To determine whether resins applied beneath the paint flake are subject to cold flow under ambient temperature conditions (10°C - 40°C).

Method: The method for determining the cold flow properties of resins has not been decided at the time of writing. Since, however, the resin is situated between the paint layer and support in a conservation situation, facsimiles of treated paint flakes will be used for testing purposes. Samples prepared as described under 2.3.3 will probably just be hung vertically, subjected to temperatures ranging from 10°C - 40°C over a prolonged period and the degree of creep of the paint flake measured.

Note on the effect of temperature on resins

The physical properties of thermoplastic resins are temperature dependent, particularly the properties of

flexibility, tack and cold flow. The significance of the Tg on the physical properties of resins has not been evaluated at this stage, however, one would expect the Tg of a suitable resin to be just below that of the ambient temperature. It is also planned to gain a more practical idea of how temperature affects the behaviour of resins. Tests for flexibility, tack and cold flow will later be undertaken at 10°C and 40°C. This represents the maximum temperature range likely to be encountered under adverse storage, display or transport conditions in Australia. (The Tg of resins will be determined, if required, by an outside laboratory using differential scanning calorimetry.)

2.3.3 RESIN APPLIED TO SIMULATED PAINT FLAKE

Tests for the resins in combination with paint and support are designed to show which of the resins work for our particular conservation application. Tests in this series are mainly subjective and are concerned with the closer evaluation of working properties, appearance and the adhesive qualities of resins.

Sample preparation:

A drawdown method, similar to the technique outlined for the preparation of resin films (2.3.2), is used to cast samples of 0.3mm thick films of paint with a thickness variation maintained at below 5%. The paint is cast onto a polyethylene release surface to enable easy removal and handling of the paint once it had set. The composition of the paint is the same as that prepared for samples used for the preliminary assessment of working properties (2.2.1).

A standard amount of resin is applied to a hardwood block and a 40mm square film of paint placed over the resin. This is gently pressed down onto the wood to simulate the flake adhesion technique and ensure even distribution of the resin. The sample is then allowed to dry for seven days at room temperature.

2.3.3.1 Appearance test

Aim: To determine how resins affect the appearance of the paint.

Method: A comparison of the paint colour before and after the resin is introduced is made, using the same measuring and observation techniques as those described in the colour tests for cured resins (2.3.2.1).

2.3.3.2 Adhesion test

Aim: To assess whether the resin achieves a reasonable bond between the paint and support.

Method: Adhesion testing and evaluation procedures have not yet been finalized.

Given the poor and variable cohesion of pigment particles and the heterogeneous nature of support materials of the artefacts for which the treatments are being developed, it is not considered that standard quantitative adhesion tests (such as the cross cut, stylus penetration or pull-off methods) would give meaningful results. The theoretical effectiveness of the adhesive bond, such as might be determined by these tests, is of much less significance than the way the adhesive is likely to perform under museum conditions.

It is anticipated, therefore, that more subjective methods will be used to assess the adhesive qualities. Resins will be applied to object facsimiles using sample preparation and flake adhesion techniques described in 1.2, 2.2.1 and 2.3.3 sections of the paper. The treated samples will be supported vertically and subjected to a series of changing RH and vibration cycles. The adhesive qualities of the resins will then be assessed subjectively by visually determining the amount of paint loss and by checking the quality of adhesion of remaining paint using a probe and stereoscopic microscope.

2.3.4 ANALYSIS OF RESINS

Aim: a) To determine the composition of resins so that those containing substances that are likely to damage objects or promote premature ageing of the resin can be eliminated from the testing programme.

b) To check formulation consistency between batches.

Method: Pyrolysis-gas chromatography-mass spectrometry will be used, based on the method developed by De Witte and Terfve²², (to be undertaken by an external laboratory).

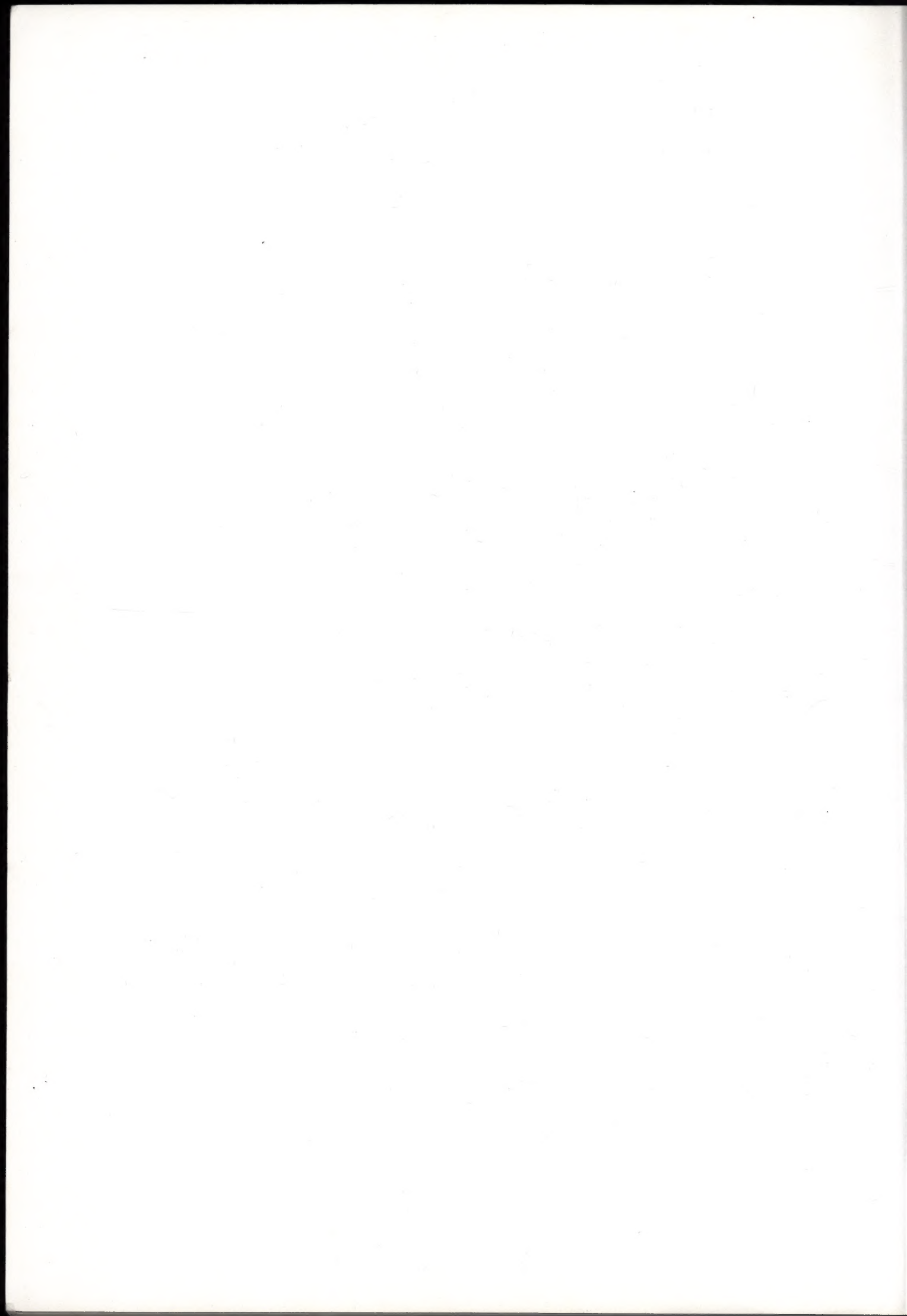
NOTES

1. Jane L. Down, "Adhesive Testing at the Canadian Conservation Institute, Past and Future," IIC Preprints of the Contributions to the Paris Congress, 2-8 September 1984, Adhesives and Consolidants, eds. N.S. Brommelle, Elizabeth M. Pye, Perry Smith and Garry Thomson, pp. 18-21.
2. Elizabeth C. Welsh, "A Consolidation Treatment for Powdery Matte Paint," The American Institute for Conservation of Historic and Artistic Works Preprints of Papers Presented at the Eighth Annual Meeting, San Francisco, California, 22-25 May 1980, pp. 141-150.
3. Anne I'ons, "Friable Ochre Surfaces: Further Research into the Problems of Colour Changes Associated with Synthetic Resin Consolidation," Institute for the Conservation of Cultural Material Bulletin 9, No. 3 and 4 (1983): pp. 13-33.
4. S. Walston and S. Gatenby, "Resin Evaluation Pilot Project Stage I, Australian Museum, Unpublished Report (1982).
5. S. Gatenby and A. Gaulton, "Resin Evaluation Pilot Project Stage II", Australian Museum, Unpublished Report (1984).
6. S. Walston and S. Gatenby, "Resin Evaluation Pilot Project Stage III", Australian Museum, Unpublished Report (1984).
7. Robert L. Feller, "Standards in the Evaluation of Thermoplastic Resins" (Paper delivered at the Fifth Triennial Meeting of the International Council of Museums Committee for Conservation, Zagreb, 1978), 78/16/4/1-11.
8. "Photochemical - Ageing Testing; Cellulose Ethers and Water-Soluble Polymers", The Getty Conservation Institute Newsletter 1, No. 1 (1986): p. 6.
9. Maureen MacDonald, "An Adhesive Testing Program Update", IIC-CG Newsletter 12, No. 2 (1986): pp. 16-17.
10. ASTM D823-84 Standard Methods of Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels, Method C - Motor-Driven Blade Film Applicator.
11. AS 2001.4.21-1979 Australian Standard Methods of Test for Textiles, Part 4 - Colour fastness Tests, Determination of Colour fastness to Light Using an Artificial Light Source (Mercury Vapour, Tungsten Filament, Internally Phosphor-coated lamp).
12. Feller, "Standards in the Evaluation of Thermoplastic Resins", p. 78/16/4/2.
13. Jane L. Down, "The Yellowing of Epoxy Resin Adhesives: Report on Natural Dark Ageing" Studies in Conservation 29, No. 2 (1984): pp. 63-76.
14. AS 1580 Method 601.1 - May 1975 Australian Standard of Test for Paints, Varnishes, Lacquers and Related Materials, Colour - Visual Comparison.
15. ASTM D1729-69 (Reapproved 1974) Standard Method for Visual Evaluation of Color Differences of Opaque Materials.
16. BS 3900: Part D1:1978 British Standard Methods of Tests for Paints, Visual Comparison of the Colour of Paints.

17. T.C. Anderson and M.J. Wright, "Development of a Colour Viewing Cabinet", Appita 25, No. 2 (1971): pp. 120-125.
18. AS 1321.7-1977 Australian Standard Methods for Sampling and Testing Adhesives, Part 7 - pH Value of Aqueous Extracts of Uncured Adhesives and of their Components, and of Cured Adhesive Films.
19. ASTM D1583-61 (Reapproved 1981) Standard Test Method for Hydrogen Ion Concentration of Dry Adhesive Films.
20. R.L. Feller and Catherine W. Bailie, "Solubility of Aged Coatings Based on Dammar, Mastic, and Resin AW-Z", Bulletin of the American Group - IIC 12, No. 2 (1972): pp. 72-81.
21. ASTM D2370-82 Standard Test Method for Tensile Properties of Organic Coatings.
22. E. De Witte and A. Terfve, "The Use of a PY-GC-MS Technique for the Analysis of Synthetic Resins," IIC Preprints of the Contributions to the Washington Congress, 3-9 September 1982, Science and Technology in the Service of Conservation, eds. N.S. Brommelle and Garry Thomson, pp. 16-18.









GETTY CENTER LIBRARY



3 3125 00920 1316

Working Groups

Page	435	Stone
	521	Theory and History of Restoration
	581	Care of Works of Art in Transit
	621	Natural History Collections
	631	Graphic and Photographic Documents
	747	Mural Paintings and Mosaics
	781	Resins

